SUDBURY ENVIRONMENTAL STUDY

SIZE DISTRIBUTION AND EMISSION RATE MEASUREMENTS OF PARTICULATES IN THE 93 M FALCONBRIDGE STACK PLUME, 1979.

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Ontario
Ministry of the Environment

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ABSTRACT

In March and September, 1979, two airborne studies were carried out in the 93 m smelter stack plume of the Falconbridge Nickel Mines Ltd at Sudbury, Ontario. A Hughes 500 C helicopter instrumented with Andersen cascade impactors and 47 mm filter packs was used to sample the plume travelling axially upwind to determine particulate size distributions and pollutant emission rates. It was found that the major emittants were $SO_4^=$, Fe, Pb, Cu, Al, As, $NO_3^=$ and NH_4^+ and the temporal variability of emissions was very large. The emitted particulates can be grouped into 2 categories - Fe, Cu, Ni, Al and Mn were associated with coarse particles with mass median diameters larger than 2.5 um; and Pb, Zn, Cd, As, $SO_4^=$ and NH_4^+ were associated with fine particles with mass median diameters less than 2.5 um.

CONCLUSIONS

Two airborne studies were carried out in March and September of 1979 in the Falconbridge 93 m stack plume to determine the sizes and emission rates of the emittants. The major findings are given below:

- Particulates measured in the Falconbridge plume can be classified into 2 categories according to the mass median diameter (MMD) - coarse particles (MMD $\geq$ 2.5 um): Fe, Cu, Ni, Al and Mn; and fine particles (MMD $<$ 2.5 um): Pb, Zn, Cd, As, SO_4 and NH_4.

- The major emittant from the stack was $SO_4^{=}$ (2.7 and 3.9 metric ton per day for the March and September studies). The chemical data, coupled with the sizing data suggest that the sulfate collected was primarily in the form of sulfuric acid. Other pollutants which were emitted in relatively high quantities as measured in the March and September studies respectively (in kg/day)were: Fe (52.1/103.8), Pb (22.9/31.2), Cu (13.0/22.0), Al (-/23.6), As (16.3/103.6), $N\text{-}NO_3^-$ (-/23.2) and $N\text{-}NH_4^+$ (-/34.4). A large temporal variability was noted, which can only be accounted for by process variation. It should be borne in mind, because of the degree of accuracy of the mass balance SO_2 emission rates used in the calculations, the reported emission rates could be underestimates of as much as 60%.

1. INTRODUCTION

From March 7 to 9 and September 7 to 11, 1979, the Special Studies Unit, as part of the Sudbury Environmental Study, carried out airborne studies of the Falconbridge 93 m smelter stack plume.

The objectives of the work were to obtain information on the size distribution of various particulate constituents of the plume and to determine emission rates of these pollutants. The former objective is very important for (i) estimating particulate deposition rates (deposition velocity being a function of particle size); (ii) identification of the origin of ambient pollutants by comparing sizing results obtained at the plume and ground levels; and (iii) assessment of potential health effects which are a function of particle size. The latter objective is necessary because at the time of the samplings no data on emission rates from Falconbridge were available since a new smelting process was adopted in the summer of 1978. In September of 1979, a joint in-stack sampling program by MOE and Falconbridge was carried out. Emissions of sulfur dioxide, sulfuric acid, particulate and trace elements as determined in that program are reported elsewhere (1).

In this report, the experimental method and results of the airborne studies are presented.

2. EXPERIMENTAL:

2.1 Airborne Sampling Instrumentation

A Hughes 500C helicopter was used as the airborne platform in both field studies. The particle measurement instrumentation was attached to a boom which extended approximately 1 metre beyond the nose of the aircraft.

The particle sizing instrumentation consisted of two Andersen 2000 Mark III Cascade Impactors. Each contained 8 impaction plates as well as a Whatman 40 back-up filter and was adapted for airborne use by attaching a rigid aluminum casing and a teflon-coated isokinetic nozzle. A picture of the impactor is shown in Figure 1. Effective cut-off diameters of these stages ranged from 0.4 to greater than 9 um.

The impaction plates in both samplers were covered with polyethylene disks to allow easy removal and analysis of the sample. One Andersen used plates covered with untreated polyethylene while the other used polyethylene coated with a thin layer of petroleum jelly. The latter was used to reduce bounce-off of large particulates as suggested by other investigators(2). The plastic disks are hereafter referred to as non-sticky (NS) and sticky substrates (SS) respectively.

All substrates and filters were cut from sheets using a stainless steel cutting die and stored in a desiccator to prevent contamination. The polyethylene substrate coating solution was prepared by dissolving 10 gm of petroleum jelly in 100 ml of toluene(2). The substrates were dipped in this solution and placed in a fume hood to allow the toluene to evaporate before loading.

The two types of substrates from the March study were subjected to analysis for all parameters of interest. Upon examination of the data, it was found (3) that the results obtained with the sticky and non-sticky substrates were not identical and the discrepancies were more serious for large particles, indicating evidence of particle bounce. Therefore, in the September study, sticky substrates were used to collect samples for trace metal analysis only and the non-sticky substrates for analysis of only $SO_4^{=}$, NO_3^{-} and NH_4^{+} (which were known to be in the small size fraction).

The instrumentation used for emission rate estimates consisted of two sets of modified Swinnex 47 mm. filter packs. Each set contained a Whatman 40 particulate prefilter and three pairs of Whatman 41 filters impregnated with a potassium carbonate-glycerol solution for trapping SO_2. A schematic of the filter packs and the actual equipment used are shown in Figures 2 and 3.

This equipment was designed to measure the in-plume ratio of metal/SO_2. This ratio, when multiplied by the known emission rate of SO_2, provides an estimate of the metal emission rate. Details of the method are discussed elsewhere (4).

Similar to the Andersen samplers, the filter pack units were attached to a teflon-coated nozzle, enclosed in an aluminum casing and bolted to both the port and starboard sides of the mounting boom. All pumps, flowmeters and rotameters were located inside the helicopter with vacuum and backflow lines (used on take-off and landing to prevent particle deposition in the nozzles) running forward to the samplers. Figure 4 shows the sampler configuration on the helicopter.

Calibrations of the flowmeters and rotameters were carried out prior to the study, and an in-flight calibration of each rotameter was done during one flight. Typical flows for the particle sizing and filter pack samplers were 29 and 13 l min^{-1} respectively.

2.2 Experimental Design

Measurement flights were designed to maximize sampling time in the plume and to achieve proper isokinetic sampling. The flights therefore consisted of a number of passes starting 4 to 5 km downwind of the chimney and moving upwind through the plume along its centreline . Air speed was maintained at approximately 13 m sec^{-1} to obtain isokinetic sampling.

A typical flying day consisted of three one-hour flights. The 47 mm filter packs were changed after each one-hour flight to prevent SO_2 saturation of the impregnated filters. These one hour flights are referred to as "runs" in the text

and the three runs in one flying day constitute a "flight".

The Andersen samplers were changed only at the end of the three runs. They therefore collected a 3 hour cumulative sample. While airborne sampling was being carried out, MOE personnel were in the Falconbridge smelter documenting smelting process operations.

On September 10, 1979, a flight sampling background air was carried out. It was found that background contributions of the various parameters of interest were negligible. Therefore no background correction was necessary in the loading calculations presented in this report.

2.3 Chemical Analysis

For the March study sample recovery of the Andersen sticky and non-sticky substrates, and Whatman 40 backup filters was similar. Substrates were placed in acid-washed 20 ml screw cap scintillation vials. Doubly distilled water (~15 ml) was added and the sample was heated at 90°C on a hot plate for 4 hours. Samples were cooled, brought to a volume of 20 ml with doubly distilled water and analyzed for sulfate by a colorimetric method. Nitric acid (0.5 ml, conc. suprapure) was added and the samples were heated at 90°C for an additional 4 hours. Samples were cooled, and brought to 20 ml with doubly distilled water before trace metal analyses. Efforts were made to analyze for Fe, Cu, Ni, Pb, Zn, Al, Cr, Cd, Mn, Co, Se, V, As, and Bi. Not all metals are reported because of non-detectable loadings (e.g., Mn, V) and contamination (e.g., Zn and Al). Due to relatively poor recovery efficiency (as determined from spike experiments), the emission results from lo-vol sampling with Whatman 40 prefilters for Pb, As, Se and Bi should be considered as lower estimates. Graphite furnace flameless atomic absorption spectroscopy was used for all metals except zinc and high iron and lead samples, where flame

absorption spectroscopy was used.

For samples collected in the September study, modified recovery procedures were adopted. The 47 mm pack Whatman 40 prefilters and the Andersen non-sticky substrates (polyethylene and Whatman 40 backup) were subjected to the same treatment. Samples were placed as received in calibrated 50 ml polyethylene centrifuge tubes. Distilled water (25 ml) was added, the tubes tightly capped and placed in an oven at 85°C overnight. There was no apparent loss of volume. The samples were well mixed and 5.0 ml taken by syringe for NO_3^-, $SO_4^=$ (Dionex - ion exchange chromatography) and NH_4^+ (colorimetry) analysis. Modifications of routine procedures were needed to allow analysis of 3 parameters on a 5 ml sample aliquot. The remaining 20 ml was acidified with HNO_3 (Suprapure, conc., 1.5 ml) and the tube resealed and again heated at 85°C overnight. The volume was adjusted to 25 ml and the solution analyzed for metals by flameless atomic absorption, and for arsenic and selenium by hydride generation atomic absorption. An arbitrary correction factor of 10% was added to the metals results to estimate the metal content of the previously removed 5 ml aliquot. This correction limits the maximum possible error to 10%.

This mild prefilter procedure is expected to give incomplete extraction for iron and aluminum. Arsenic and selenium values may be up to 25% high because of valence state uncertainty. Cadmium results may be systematically 50% low because of poor recovery as indicated by laboratory spike experiments..

The Andersen sticky substrates (polethylene) and Whatman 40 backup samples were placed in teflon tubes and low- temperature ashed for several days. In some samples not all the polyethylene filter had disappeared after this time; HNO_3 (conc. 1.5 ml) was added and the volume brought to 25 ml with distilled water. The tubes (screw top, Oak Ridge type) were capped and the samples placed in a hot block at 150°C for 16 hours. Water vapor escaped despite the threaded top and after 16 hours 1 ml remained. The tubes were cooled, brought to 25 ml with distilled water, mixed and analyzed for metals by flameless a.a.s.

The low temperature ashing - acid digestion procedure has been found to give good recoveries for all elements except Al which amounts to only 1/3 - 1/8 of the total Al actual loading. Low temperature ashing volatilized arsenic and selenium; thus, these elements were not determined.

As mentioned earlier the filter pack samplers each contained a Whatman 40 filter followed by three pairs of impregnated Whatman 41 filters. The impregnated Whatman 41 filters trapped SO_2 by converting it to SO_3. Extraction of these filters with 0.05% H_2O_2 converts the $SO_3^=$ to $SO_4^=$ and allows this extract to be analyzed directly by ion exchange chromatography . The results indicate very good SO_2 sampling efficiency; in general, less than 1% of the loading was found on the second pair of filters and a negligible amount was present on the third pair of filters.

2.4 Scanning Electron Microscopy (SEM) Analysis

The non-sticky substrate samples from Flight #2 of the March study were stored in petri dishes rather than in polyethylene bags upon unloading. This allowed the individual samples to be examined under scanning electron microscope.

Visible dots were obvious only on the last stages of the Andersen samples. An examination under a microscope was necessary to locate particles on the balance of the substrates. Even so, no definitive dots were observed on stages 1 and 2. On both stages 0 and 3, particulates of various sizes exhibiting an undefined pattern were observed under the microscope, and the samples for SEM analysis were cut from the centre of the substrate. A very well defined impaction pattern was observed on stages 4 and 5. There was evidence of substrate shifting from the impaction plate at stages 6 and 7. It is very interesting to note that the dots on stages 5 to 7 were reddish in colour, and were probably due to the presence of hygroscopic $SO_4^=$ and either ferric sulfate or ferric hydroxide.

A visible impaction dot from each polyethylene substrate stage was cut out

and the substrate was handled with platinum tweezers. The cut sample was then adhered to a carbon stub and coated with a silver paint before an evaporation process was carried out. The backup Whatman 40 cellulose filter was unsuitable for SEM analysis.

Details of the SEM results are reported elsewhere (3). The results, however, are summarized briefly below. On the upstream stages, the major constitutents were S, Fe and Si with the presence of smaller quantities of K, Ca, Ti, Ni, Cu, Zn and Pb. There was also evidence of trace amounts of Al and Mg. On the last two stages, little trace metal loading was present and the content was dominated primarily by sulfur compounds which were most likley non-metal sulfates such as sulfuric acid and ammonium sulfate.

Comparisons of the expected and observed particle sizes (see Table A11 in the Appendix) suggested that particle bounce-off of larger size trace metal particulates and condensation and/or crystallizaiton of the sulfur species had taken place after collection.

It should be noted again that this analysis was carried out on non-sticky substrates and these SEM analysis results, coupled with the detailed chemical analyses, pointed to the fact that bounce-off problems did occur with non-sticky substrates under airborne sampling conditions. This was especially serious with particles in the coarse size range. Since the non-sticky substrate samples do not necessarily yield information on the true particle size distribution for large particulates, and the sticky substrate samples are not suitable for SEM analysis, it is concluded that the information generated by the SEM technique on the Andersen samples, except for particles in the submicron size range, should be regarded as qualitative only.

In view of this, SEM analysis was not repeated for the September samples.

3. DATA PRESENTATION

3.1 Flow Data

Flow rates, and flow volumes for both the 47 mm filter pack samples and the Andersen impactor samples for the two studies are summarized in the Appendix as Tables A1 and A2.

A detailed analysis of the flow rates throughout each flight of the March Study has shown evidence of a small leak in the port 47 mm filter pack during the third run of Flight 1. It appears that the particulate filter developed a break midway through the run; however, subsequent scrutiny of the data indicated that the leak did not result in significant systematic errors in the analysis.

For the September study, the loadings on the last set of filters for both Flights #2 and #4 were relatively low because of low smelter emissions and therefore short sampling time. The loading of the last run of the latter flight was especially low and therefore data from this run were not included in emission rate calculations reported in Section 4.2.3.

3.2 Emissions from Production Data

Throughout each flight, the converter operation within the Falconbridge smelter was monitored. The SO_2 emission rate is extremely sensitive to the frequency of converter operation.

From a knowledge of the number of converters operating and the smelter daily mass balance, SO_2 emission rates for the individual runs were estimated and these are given in Tables A3 and A4 in the Appendix for the March and September studies respectively. The average SO_2 emission rates for the two sampling periods were approximately 170 and 210 MTPD (metric ton per day). It is expected that full operation with 2 converters will result in an SO_2 emission rate of 400 MTPD.

3.3 Chemical Analysis Results

The results from the chemical analysis of 47 mm filter pack samples are presented as concentrations and particulate-to-SO_2 ratios in Tables A5 to A8 in the Appendix according to sampling dates, runs and sampler location. Only data which correspond to sample loadings higher than or equal to two times the filter blank values are given.

The Andersen data are also tabulated in terms of concentration per stage in Tables A9 and A10. The effective cut off diameters of these stages are given in Table A11. Concentrations appear to be somewhat higher in the September study and the discrepancies may be partially due to the different chemical analysis techniques used in the studies.

3.4 Precision of Data

Data were evaluated in terms of (i) Precision of data measured by port and starboard 47 mm samplers, (ii) Sticky-and non-sticky Andersen substrate loadings and (iii) 47 mm vs. Andersen impactor loadings.

Consistency in the 47 mm port and starboard concentrations was quite good in general and the details are given elsewhere (3, 5). Sulfur dioxide and sulfate show the best agreement from port to starboard while cadmium shows the poorest agreement. Cu, Ni, Fe and Pb are intermediate and vary typically with $\pm$ 50% for the March study. The agreement in the September Study is somewhat better.

In the March study, it was noted that the smallest particulates, viz, Pb, As and $SO_4^{=}$, as well as Cu, had significantly greater total loadings in the non-sticky Andersen sampler. The other parameters except for Cu, Ni, Zn, did not show consistently higher loadings in the sticky or non-sticky sampler. This may indicate either a particle bounce-off problem with the non-sticky substrates for large particulates, or possible analytical problems with small particulate and sticky

substrates. Thus in the September study, sticky substrates were used for trace metals and non-sticky substrates for major ions analyses.

In the March study, a comparison between Andersen and 47 mm samplers shows a significant difference in flow-normalized loadings (i.e. average plume concentrations) determined by the 2 types of sampler. In general, the Andersen samplers have significantly lower concentrations than the 47 mm pack. This is not uncommon in particle sizing versus total filter sampling and has been reported by other workers (6). It is unclear if this is an inherent difference in the two sampling methods or if it resulted from problems associated with the helicopter installation. However, the situation was improved in the September study(5). Because of the higher confidence that can be placed on the 47mm sampling method, values thus obtained were used in the emission rate calculations.

4. RESULTS AND DISCUSSION

4.1 Particle Sizing Experiments

4.1.1 Introduction

An excellent description of aerosol sizing data presentation has been given by Whitby (7) where it is shown that cumulative plots are quite useful in determining the aerodynamic mass median diameter of a sample. This approach however has some limitations in that the median obtained represents a rough average of the fine and coarse modes and it hides the modal characteristics of the distribution. However, for deposition calculation purposes, data generated by this techique are sufficient.

An alternative plotting method is the differential plot which shows the different "modes" of particle size; it indicates the amount of the sample which is found in each size range along a continuous spectrum. This latter plot has the advantage over the cumulative plot approach when data for some stages are missing. If a linear plotting co-ordinate is used, the ratio of modal areas underneath the modes could potentially be used as an indicator for particle source identification.

4.1.2 March Study Results

Figures 5 to 14 are size distribution probability plots of the trace metals (with sticky substrates) and $SO_4^=$ (with non-sticky substrates) as observed in the March study. As discussed earlier, non-sticky substrates yielded incorrect heavy metal data and are therefore not included. The determined aerodynamic mass median diameters are summarized in Table 1.

The corresponding differential plots ($\Delta m/\Delta \log Dp$ vs. Dp) and summary data are given in Figures 15 to 24 and Table 2.

4.1.3 September Study Results

As noted earlier, based on experience gained in the March study, trace metal loadings were determined on sticky substrates and major ions on non-sticky substrates.

Both types of plotting methods were used and the data are represented in Figures 5 to 24 and Tables 1 to 2 together with the March data.

4.1.4 Comparison of March and September Results

Some general observations can be made of the 2 studies:

1. The species measured can be classified into 2 categories according to the mass median diameters (MMD):

   (a)Coarse particles (MMD > 2.5 um): Fe, Cu, Ni, Al, and Mn

   (b)Fine particles (MMD < 2.5 um): Pb, Zn, Cd, As, $SO_4^=$ and NH_4^+.

   The aluminum results should be accepted with reservation because the Andersen sampler is made of aluminum, and thus contamination is probable.

   Large departures from log-normal size distribution are frequently observed in our results. Some of these may be only apparent due to difficulties in chemical analysis of very lightly loaded impactor substrates. Others may be a reflection of bimodal or trimodal characteristics which are exemplified in the differential plots. The unusually high MMD's for Fe, Cu and Ni are somewhat unexpected and may be linked to the efficiency of the electrostatic precipitator.

2. The maxima determined from the differential plots for the 2 studies showed reasonably good consistency. Most particles display modes at about 0.4 to 0.7 um and 2 to 3 um, and some have a third one around 5 um. There is also evidence of a mode larger than 9 um for some

heavy metals; however, this information is concealed due to the upper sampling limit of the sampler.

4.1.5 Comparison of Airborne vs In-Stack Measurements

In September, 1979, three single-point in-stack particle sizing experiments were carried out at the 93 m Falconbridge stack. Although none of these runs coincided with the airborne flights, a comparison of the data is still interesting.

The in-stack sizing results are summarized in Table 3 for some selected parameters. It should be noted at this point that no direct comparison of in-stack and helicopter sizing instrumentation has been carried out. Therefore, differences in the results of the two methods as reported here may or may not be significant. The following discussion is based upon the assumption that the methods are equivalent but caution should be exercised in the interpretation. In general, it seems that the size of larger particulates containing Fe, Ni and Cu increases upon release into the atmosphere. Particulates containing volatile metals such as Pb and Zn remain fairly consistent. In the case of $SO_4^=$, an unexpected phenomenon was observed, i.e. the size of the $SO_4^=$ particulate is apparently reduced upon release into the atmosphere. It is suspected that this may be due to sampling and analytical problems associated with the in-stack measurements. In the in-stack Andersen Sampling, glass fibre filters were used and spurious sulfate formation due to SO_2 passage through the filter could potentially change the real size distribution. It has been also recognized that sizing measurements of sulfuric acid inside the stack using the existing method may not yield accurate results. If the in-stack sampling train collects preferentially non-volatile metal sulfates but not sulfuric acid due to the high sampling termperature, this could potentially result in a larger MMD of the sample and a lower emission rate of $SO_4^=$ as trace metal sulfates are in larger particle size range than sulfuric acid. However, under airborne sampling conditions at ambient temperature, sulfuric acid which is in the

fine particle size range, will be in the form of aerosol and will be collected without loss on the substrate. Due to the potential loss of sulfuric acid, the in-stack $SO_4^=$ particle size distribution will be biased towards the coarse particle size range and the $SO_4^=$ emission rate measured will also be reduced artificially.

4.2 Pollutant Emission Rate Estimates

4.2.1 Introduction

The 47 mm filter pack system was used to sample particulates and SO_2 simultaneously . The resulting ratios of particulate-to-SO_2 can be multiplied by the known SO_2 emission rate to obtain the metal emission rate. A discussion of the feasibility of this method is given elsewhere (4) and it appears that average metal emission rates can be suitably estimated in this manner.

In order to obtain the particulate emission rates (E.R.), calculations were done using two different approaches. The first approach required calculation of particulate emission rates for each individual sampling run (see Tables 4 and 5) before averaging and the second approach required calculation of the average particulate-to-SO_2 ratio before multiplying by the average SO_2 emission rate. The two formulae are given below:

Method 1:
$$\frac{\sum_{i=1}^{n}\left[\left(\frac{M}{SO_2}\right) \times (SO_2)_{E.R.}\right]_i}{n} \qquad (1)$$

and

Method 2:
$$\left[\frac{\sum_{i=1}^{n}\left(\frac{M}{SO_2}\right)_i}{n}\right] \times \left[\frac{\sum_{i=1}^{n}(SO_2)_{i,E.R.}}{n}\right] \qquad (2)$$

where n = the number of runs

i = individual run number

ER = emission rate

In general, the agreement between the two methods was quite good.

4.2.2 March Study Results

The results obtained using the 2 methods for the March study are summarized in Table 6. During this study, 3 flights each consisting of 3 runs were carried out. It can be seen from Table 4 that the emission rates of the various species are not constant over the sampling period and measurements during successive runs can differ by as much as a factor of ten. It is expected that short-term process variations are the cause of this large temporal variability which is reflected in the standard deviations given in Table 6. As mentioned in Section 2.3, due to chemical analysis problems, Pb, As, Se, and Bi values probably represent lower limits.

4.2.3 September Study Results

During the September study, only two flights were carried out, each consisting of three runs. Because of the limited sampling time during the third run of the second flight, only small amounts of sample approaching the chemical detection limits were collected. Therefore values from this run were not included in the calculations.

Results of emission rates determined using both methods 1 and 2 are summarized also in Table 6. Again, temporal variability is rather large. Because of the sample-extract split for analysis of trace metals and other parameters (see Section 2.3), errors up to 10% can be expected. Also, it was pointed out that emission rates of Al and Cd were systematically low, and As and Se systematically high (by up to 25%) due to analytical difficulties.

4.2.4 March vs. September Results

The sampling results indicate that the major emitted pollutant is $SO_4^=$. This sulfate is most probably in the form of H_2SO_4 as suggested by the sizing and chemical results. Other major emittants are Fe, Pb, Cu, Al and As. It was somewhat unexpected to see the extremely high arsenic emissions during one of the September flights. It has been observed in another MOE study (8) that the As content of soil near Falconbridge is unusually high, on the order of 200 to 300 ppm. This may be due to local deposition of the smelter emissions. It should be further pointed out that the reported As emissions are probably underestimates as the sampling method does not retain vapour phase As species. Both NO_3^- and NH_4^+ were measured in the September study and the amounts detected were not negligible.

The SO_2 emission rate was about 25% greater in the September study. The particulate-to-SO_2 ratios were also higher in September except for Pb, Cd and Se. Parameters with most notable increases in emission rates were Fe, Cu, Ni, As, and $SO_4^=$. The Cd emission rate was lower by almost a factor of ten and Se by a factor of four. The large variation in emission rates from study to study is seen to be quite large. It cannot be explained by the chemical analysis problems encountered, and therefore must be related to process variability. .

Comparisions of the emitted metal and sulfate quantities with the corresponding SO_2 values indicated no simple relationship. Tables 7 and 8 are summary tables showing the linear cross-correlation coefficients of metal-to-SO_2 ratios as observed on the 47 mm filters, and average plume concentrations of metal and SO_2 respectively. In both Tables the SO_2 emission rates estimated from converter operation were also included in the correlation. The former (Table 7) takes into account the SO_2 production and the latter (Table 8) shows the absolute relationship among the various parameters. Only correlation coefficients significant at the 99% confidence level are printed.

It is noted that regardless of the source conditions, there is a high correlation between 4 trace metals, namely, Fe, Cu, Ni and Pb. The fact that Fe, Cu, and Ni are highly correlated is not surprising because these are major metals characteristic of smelter operation. Pb and As are variables depending on the mix of Strathcona/Falconbridge concentrate which by itself is a variable(9). Therefore, Pb cannot be expected to correlate well with Fe, Cu, and Ni. The high correlation observed is thought to be fortuitous. Fe, Cu, Ni and Pb may be highly correlated with $SO_4^=$ because they may exist largely as metal sulfates. As, Pb and $SO_4^=$ correlation might depend on fume generation and subsequent gas temperature history. Other, somewhat ambiguous, high correlations such as As, Se and trace metals, $SO_4^=$ and NH_4^+ are difficult to interpret. The high correlation between the concentrations of SO_2, Cu, Ni and $SO_4^=$ may suggest that these species are produced and emitted in similar processes. The reason for the correlation between SO_2 and Pb, and As and Se could possibly be the same, but most likely is a result of high cross correlation between $SO_4^=$, Pb, As and Se.

4.2.5 Airborne vs. In-Stack Measurements

During the September study, on September 9th, multi-point in-stack source testing were carried out by the MOE Source Assessment Unit (1). A comparison of the airborne and in-stack emission rate is made in Table 9. Average emission rates for the total study determined from in-stack particulate/acid tests are included for comparison.

In stack particulate measurements yielded higher emission rates of Fe, Cu, Ni, Zn and Cd, and very much lower rates of As and $SO_4^=$. In the case of As and $SO_4^=$, it is speculated that due to the relatively high temperature in the stack and the volatility of these species, not all the As and H_2SO_4 were collected in the stack tests. As a result of this, the airborne emission rates of these species are

higher than those measured in-stack. Part of the discrepancies can be explained by the fact that the airborne sampling was carried out over a much shorter interval as compared to the in-stack measurement and was subject to a larger impact of the process variation. This is reflected by the relative magnitude of the standard deviations of the two types of measurement. If the range of emission rates is considered, it is noted that most of the measurements agree reasonably well. It is also noted that average particulate/acid test data for Fe, Cu, Ni and Al are in reasonable agreement for the two types of measurement.

However, it appears that the largest source of error in the airborne emission rate estimates is in the SO_2 emission rate values used in the calculations. One may recall that emission estimates were obtained by multiplying the particulate -to - SO_2 ratio by the SO_2 emission rate based on mass balance calculations. It is obvious that the particulate emission rates can only be as accurate as the SO_2 emission rate used in the calculation.

Based on the one day for which simultaneous in-stack and mass-balance SO_2 measurements were available, discrepancies in the SO_2 emission rate of 10 to 60% were noted. The balance estimates were consistently lower than the in-stack measurements. Therefore, in comparing the airborne and in-stack measurements, this relative accuracy must be considered.

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Table 1: Mass Median Diameter* (um) by Andersen Sampling in the Falconbridge Smelter Plume

	March 1979			September 1979	
Flight	1	2	3	1	2
Parameter					
Fe	> 9	>9	8.65	7.1	7.0
Cu	> 9	7.35	8.20	5.9	4.4
Ni	> 9	> 9	>9	>9	6.6
Pb	0.92	1.01	0.87	0.95	-
Zn	>4.7	1.90	1.00	0.84	-
Al^{+}	-	5.40	-	7.2	2.9
Mn	-	-	-	5.5	-
Cd	< 0.7	1.09	0.93	5.3	2.3
As	0.89	0.67	0.69	-	-
SO_4	0.60	0.59	0.62	0.82	0.64
NH_4	-	-	-	0.7	0.84

* All parameters were determined from sticky polyethylene substrates except SO_4 and NH_4 which were determined from non-sticky polyethylene substrates.

\+ Probably contamination due to Al sampler.

TABLE 2: SUMMARY OF MODAL DIAMETER (um) FROM AIRBORNE SAMPLING IN THE FALCONBRIDGE SMELTER STACK PLUME*(1979)

	Mar. 7	Mar. 8	Mar. 9	Sept. 9	Sept. 11
Fe	2.5, 4.7	0.9, 2.6	0.7, 3	1.2, 3.5	--
Cu	0.4, 2, 4.7	0.7, 2.2	0.7	0.9, 2.7	1.9
Ni	0.4, 2, 4.7	0.7, 3.3	1.1	1.1, 3.5	0.3
Pb	0.7, 4.7	0.7	0.7, 3.3	0.7, 4.7	--
Zn	0.4, 1.1, 4.7	0.7, 3.3	0.7, 3.3	0.7, 2.1, 4.7	--
Al	0.4, 2.1	0.8, 2.1, 4.7	1.7, 5	--	0.7, 2.1
Cd	0.4, 2.5	0.7	0.7, 2.1	0.7	0.7, 2.1, 4.7
As	0.6	0.7, 2.1	0.7, 3.3	--	--
NH_4	--	--	--	0.7, 2.5, 4.7	0.7, 3.3
SO_4	0.6	0.7	0.6	0.7, 3.3	0.6

* There is evidence of a mode larger than 9 um for some heavy metals; however, this information is concealed due to the upper sampling limit of the sampler.

Table 3: Comparison of Mass Median Diameter (um) of Particulates Determined by In-Stack and Airborne Measurements at the 93 m Falconbridge Stack in 1979

Parameter / Test	Fe	Ni	Cu	Pb	Zn	SO_4
In-stack (Sept.)						
#1(Aug. 28)	4.5	5.5	4.6	.58	.70	4.3
#2(Aug. 29)	3.5	3.9	3.1	.60	.68	2.2
#3(Aug. 30)	7.3	6.8	4.75	.70	.94	3.5
Airborne (Sept.)						
#1(Sept. 9)	7.1	9	5.9	.95	.84	.82
#2(Sept. 11)	7.0	6.6	4.0	-	-	.64

Table 4: Summary of Calculated Emission Rates from the Falconbridge Smelter Stack During March /79 Study* (kg/day)

Flight	Port/ Starboard	Parameter										
		Fe	Cu	Ni	Pb	Cr	Cd	Co	Se	As	Bi	SO_4
1 (Mar. 7)	P	69.1	8.82	13.8	40.2	-	36.5	-	6.3	21.4	-	5548
	P	177.8	45.4	32.1	47.3	-	15.2	-	9.5	22.7	-	5101
	P	-	4.6	3.2	6.7	-	-	-	2.1	-	-	1681
	S	-	24.6	13.7	39.7	-	-	-	9.6	32.8	-	6566
	S	101.8	36.9	19.3	43.8	-	-	-	-	-	-	2972
	S	-	4.3	2.4	6.2	-	-	-	-	-	-	1795
2 (Mar. 8)	P	26.1	7.4	3.5	14.7	-	6.6	-	-	17.9	-	1831
	P	77.0	18.4	10.7	28.6	0.5	6.3	0.5	-	22.0	-	1974
	P	-	2.5	1.2	4.0	-	-	-	-	2.5	-	1386
	S	27.1	7.7	4.5	18.9	-	3.6	-	-	16.2	-	2567
	S	74.2	20.2	11.5	28.3	-	2.4	0.5	-	17.7	-	2096
	S	10.9	4.9	1.4	4.3	-	-	-	-	1.6	-	1395
3 (Mar. 9)	P	43.8	14.6	5.7	32.9	-	5.5	0.2	1.0	23.1	1.6	3536
	P	-	4.6	2.1	11.9	-	-	-	-	7.3	-	2440
	P	11.7	4.5	1.9	11.2	-	1.2	-	-	10.4	-	1309
	S	21.0	14.9	4.2	30.9	-	7.3	-	2.3	29.2	2.0	3094
	S	12.2	5.6	2.4	23.8	-	23.8	0.4	1.5	10.4	-	2176
	S	13.4	4.8	2.9	19.3	-	22.8	-	1.3	9.0	-	1494

* Only samples with loadings equal to or greater than 2x filter blank values were used in calculations.

Table 5: Summary of Calculated Emission Rates from the Falconbridge Smelter Stack During September /79 Study (kg/day)

Flight	Port/ Starboard	Parameter												
		Fe	Cu	Ni	Pb	Zn	Al	Mn	Cd	As	Se	$N\text{-}NO_3$	$N\text{-}NH_4$	SO_4
1 (Sept. 9)	P	35.63	6.23	3.26	6.66	-	-	-	1.41	51.14	.67	-	-	1877
	P	216.3	65.72	31.25	52.58	4.12	29.51	.82	2.47	295.1	1.23	6.57	21.38	6101
	P	33.23	12.62	6.81	36.18	-	-	-	-	114.4	1.60	72.36	37.79	5789
	S	43.38	7.73	8.42	9.55	-	13.87	.43	-	43.38	.52	-	-	2026
	S	260.4	60.02	57.54	59.27	5.61	27.28	.80	2.08	285.2	1.52	6.40	-	6770
	S	102.4	13.45	6.89	41.0	-	-	-	-	114.2	1.46	7.32	43.95	5414
2 (Sept. 11)	P	129.0	19.53	11.66	44.06	-	-	-	2.83	47.23	1.26	-	-	4147
	P	26.31	5.53	3.23	9.23	-	-	-	.40	10.81	.40	-	-	1487
	S	157.5	23.30	13.22	44.06	-	-	-	-	65.95	.94	-	-	4406
	S	33.51	6.16	4.45	9.36	-	-	-	-	8.34	.31	-	-	1440

* Only samples with loadings equal to or greater than 2x filter blank values were used in calculations.

Table 6: Estimated Emission Rates of Pollutants from the 93 m Falconbridge Smelter Stack (kg/day)

	Fe	Cu	Ni	Pb	Zn	Al	Mn	Cd	As	Se	$N\text{-}NO_3$	$N\text{-}NH_4$	SO_4	Cr	Co	Bi
March, 1979																
N*	13	18	18	18	-	-	-	11	15	8	-	-	18	1	4	2
Method "1"																
A.V.	51.2	13.0	7.6	22.9	-	-	-	11.9	16.3	4.2	-	-	2720	0.5	0.4	1.8
S.D.	48.7	12.1	8.1	14.2	-	-	-	11.3	9.3	3.7	-	-	1542	-	0.14	0.3
Method "2"	43.5	11.6	6.6	20.5	-	-	-	10.4	14.1	3.3	-	-	2587	0.6	0.5	1.4
September 1979																
N*	10	10	10	10	2	3	3	8	10	10	4	3	10	-	-	-
Method "1"																
A.V.	103.8	22.0	14.7	31.2	4.9	23.6	0.7	1.8	103.6	1.0	23.2	34.4	3946	-	-	-
S.D.	84.9	22.4	17.2	20.4	1.1	8.5	0.2	1.0	104.6	0.5	32.8	11.7	2074	-	-	-
Method "2"	94.7	20.1	13.6	27.7	4.1	23.2	0.7	1.6	93.3	0.9	18.4	27.4	3717	-	-	-

*N = number of samples

TABLE 7: FALCONBRIDGE PLUME STUDIES (March & September 1979)
PARTICULATE-TO-SO_2 RATIOS DATA
LINEAR CORRELATION COEFFICIENT
99% CONFIDENCE LEVEL
(# OF OBSERVATION PTS)

	Fe	Cu	Ni	Pb	Zn	Al	Mn	Cd	Cr	Co	Bi	As	Se	NO_3	NH_4	SO_4	SO_2*
Fe	1.000 23																
Cu	0.908 23	1.000 28															
Ni	0.923 23	0.905 28	1.000 28														
Pb	0.734 23	0.772 28	0.721 28	1.000 28													
Zn					1.000 2												
Al						1.000 3											
Mn							1.000 3										
Cd								1.000 19									
Cr									1.000 1								
Co										1.000 4							
Bi											1.000 2						
As	0.725 22	0.758 24	0.730 24	0.533 24								1.000 24					
Se													1.000 18				
NO_3														1.000 4			
NH_4															1.000 3		
SO_4	0.686 23	0.540 28	0.599 28									0.730 24				1.000 28	
SO_2*				0.680 28													1.000 28

* SO_2 emission rates determined from mass balance calculations.

TABLE 8: FALCONBRIDGE PLUME STUDIES (March & September 1979)
CONCENTRATION DATA
LINEAR CORRELATION COEFFICIENT
99% CONFIDENCE LEVEL
(# OF OBSERVATION PTS)

	Fe	Cu	Ni	Pb	Zn	Al	Mn	Cd	Cr	Co	Bi	As	Se	NO_3	NH_4	SO_4	SO_2	SO_2*
Fe	1.000 23																	
Cu	0.858 23	1.000 28																
Ni	0.806 23	0.928 28	1.000 28															
Pb	0.832 23	0.870 28	0.739 28	1.000 28														
Zn					1.000 2													
Al						1.000 3												
Mn							1.000 3											
Cd								1.000 19										
Cr									1.000 1									
Co										1.000 3								
Bi											1.000 2							
As	0.852 22	0.924 24	0.838 24	0.946 25								1.000 24						
Se	0.632 16	0.703 18		0.933 18								0.858 16	1.000 18					
NO_3														1.000 4				
NH_4															1.000 3			
SO_4	0.783 23	0.839 28	0.714 28	0.984 28								0.952 24	0.939 18			1.000 28		
SO_2	0.765 23	0.807 28	0.665 28	0.977 28								0.911 24	0.933 18			0.988 28	1.000 28	
SO_2*																		1.000 28

* SO_2 emission rates determined from mass balance calculations.

Table 9: Comparison of Instack vs Airborne Emission Rates (Sept. 9, 1979) in kg/day

	Parameter									
	Fe	Cu	Ni	Pb	Zn	Al	Mn	Cd	As	SO_4
Airborne (Sept. 9, 1979)										
Flt 2 Method 1	115.2	27.6	19.0	34.2	4.9	23.6	0.7	1.5	150.6	4663
Flt 2 Method 2	105.9	24.9	17.4	30.2	4.2	23.3	0.7	1.6	136.7	4304
Instack										
Sept. 9, 1979	362.0	42.3	35.4	28.5	7.8	6.1	0.5	3.3	40.6	670.5
3 Particulate/Acid Test Average (Sept. 1979)	207.9 ±134.0	26.0 ±14.1	20.2 ±13.2	44.9 ±20.8	9.5 ±3.0	34.6 ±25.0	0.3 ±0.2	5.0 ±1.5	25.1 ±18.1	728.4 ±387.3

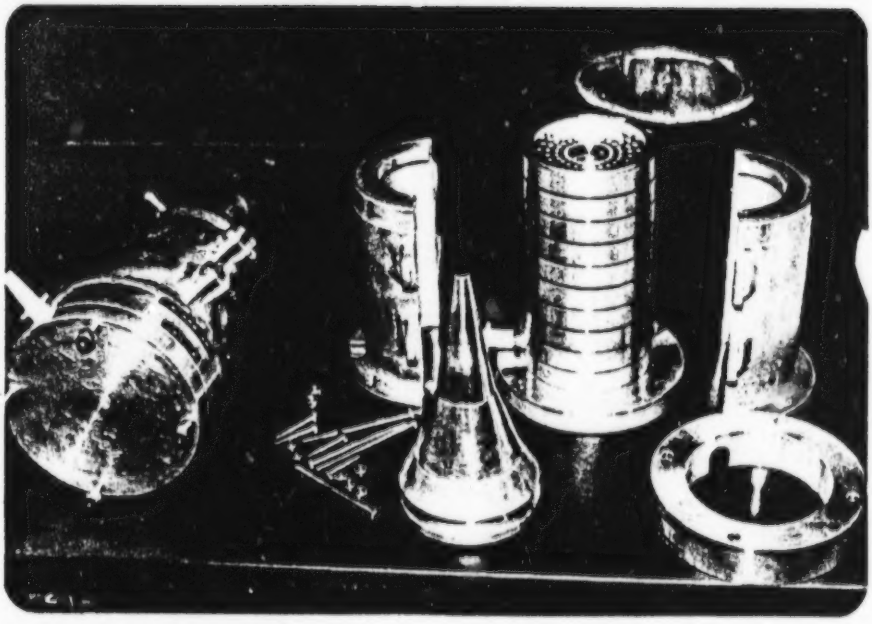


FIGURE 1

Andersen Cascade Impactor Shown with
Casing Used in Airborne Study

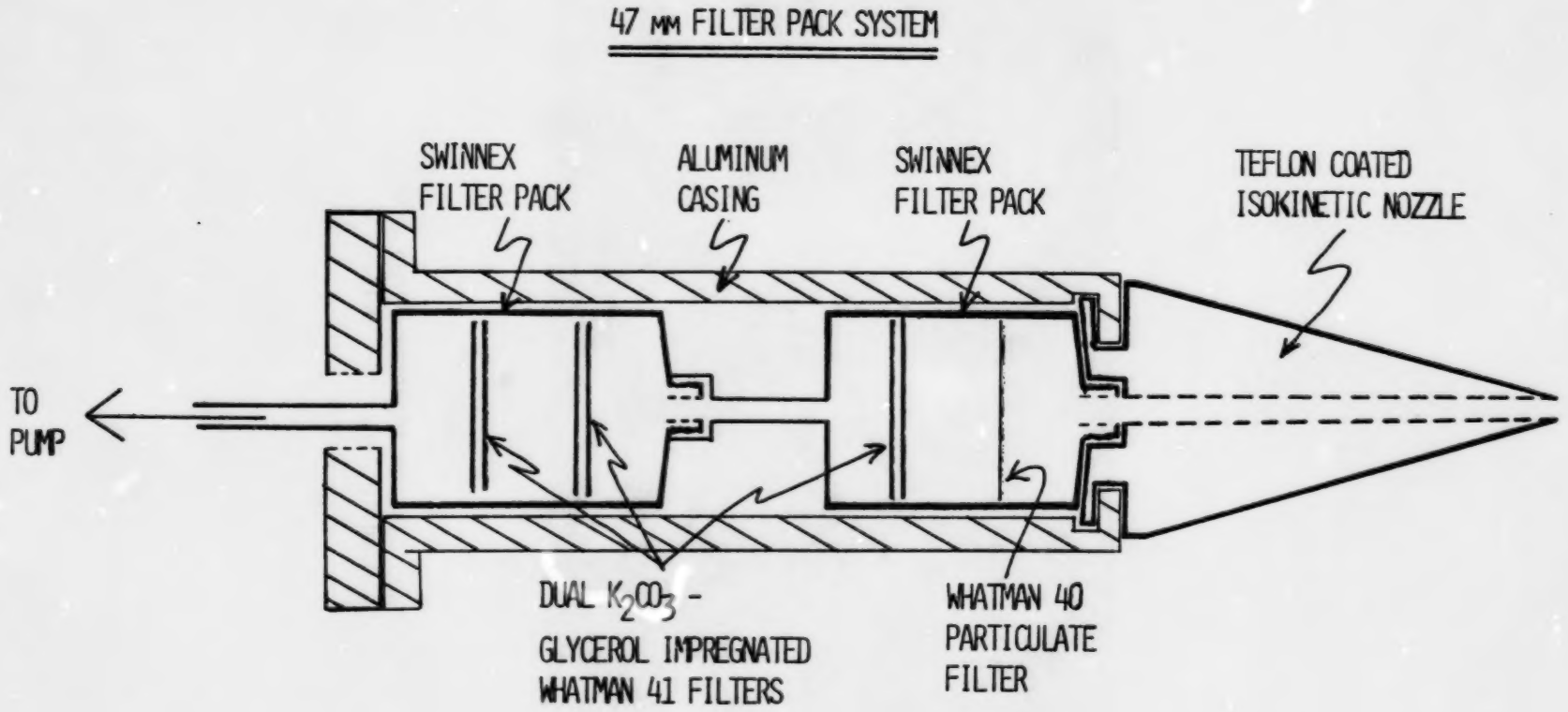


FIGURE 2

A Schematic Diagram of the 47 mm Filter Packs

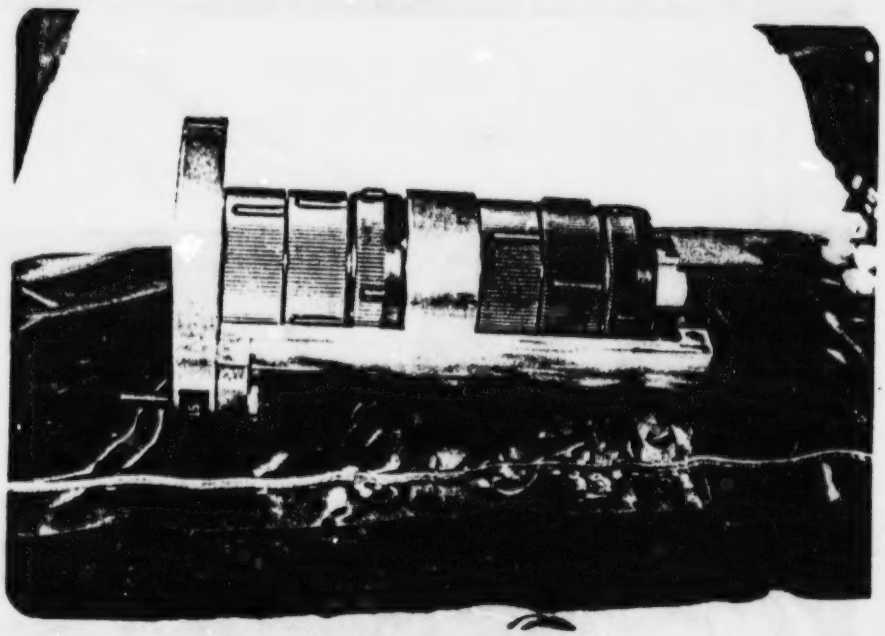
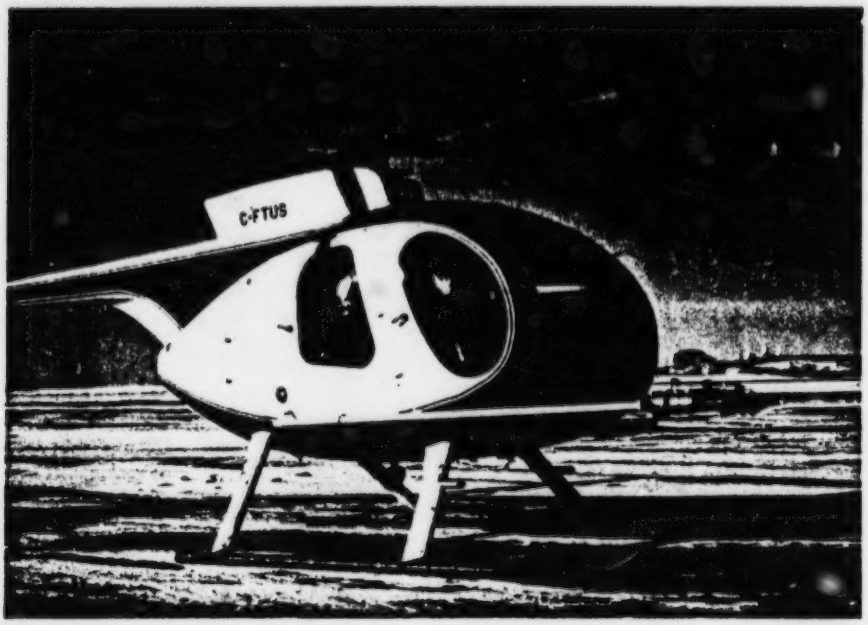


FIGURE 3 -- 47 mm Filter Packsin Casing

(a)



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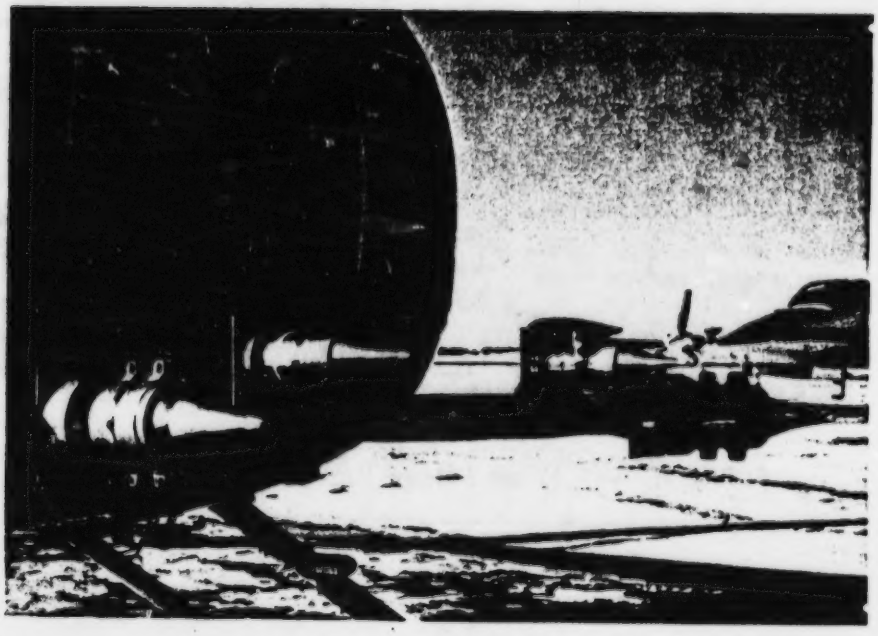


Figure 4: Instrumented Aircraft Used in The Airborne Studies (Anderson cascade impactors mounted on extreme left and right, and 47 mm. filter packs mounted in centre)

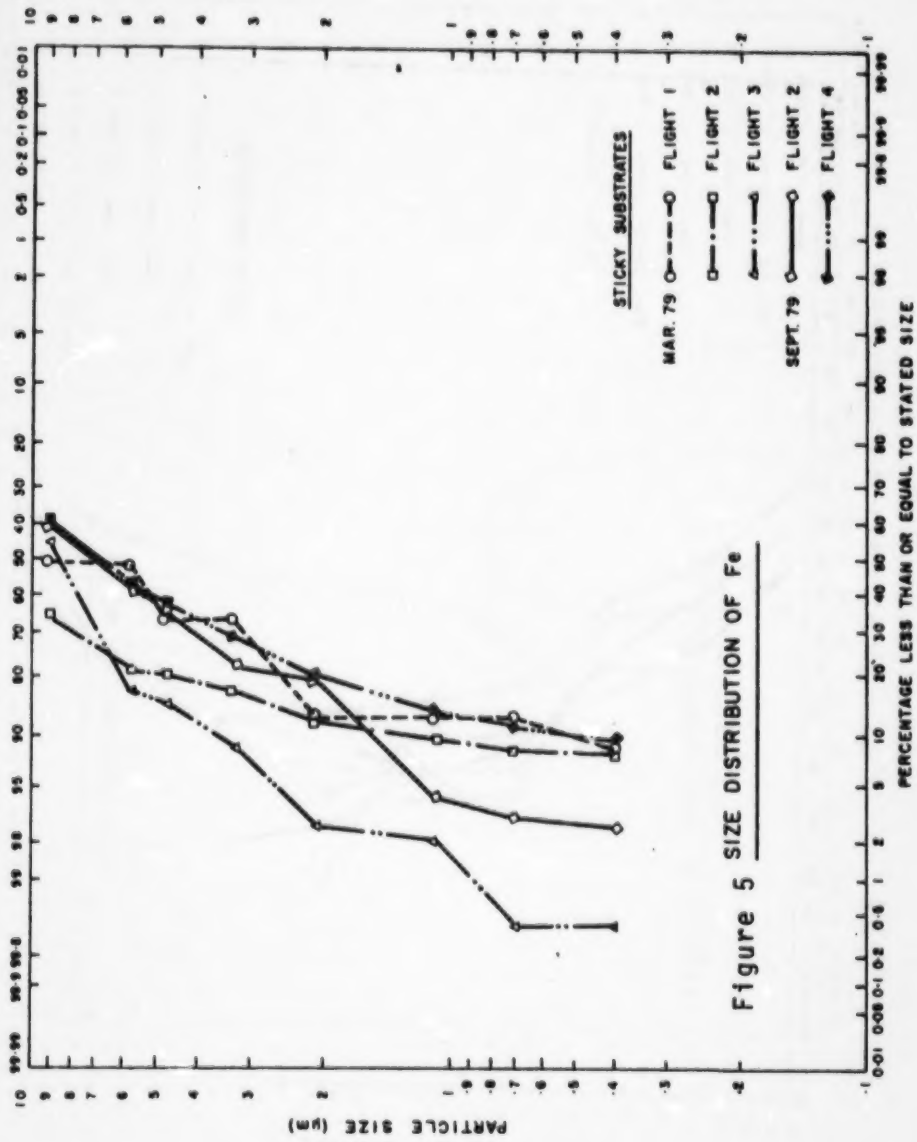


Figure 5 SIZE DISTRIBUTION OF Fe

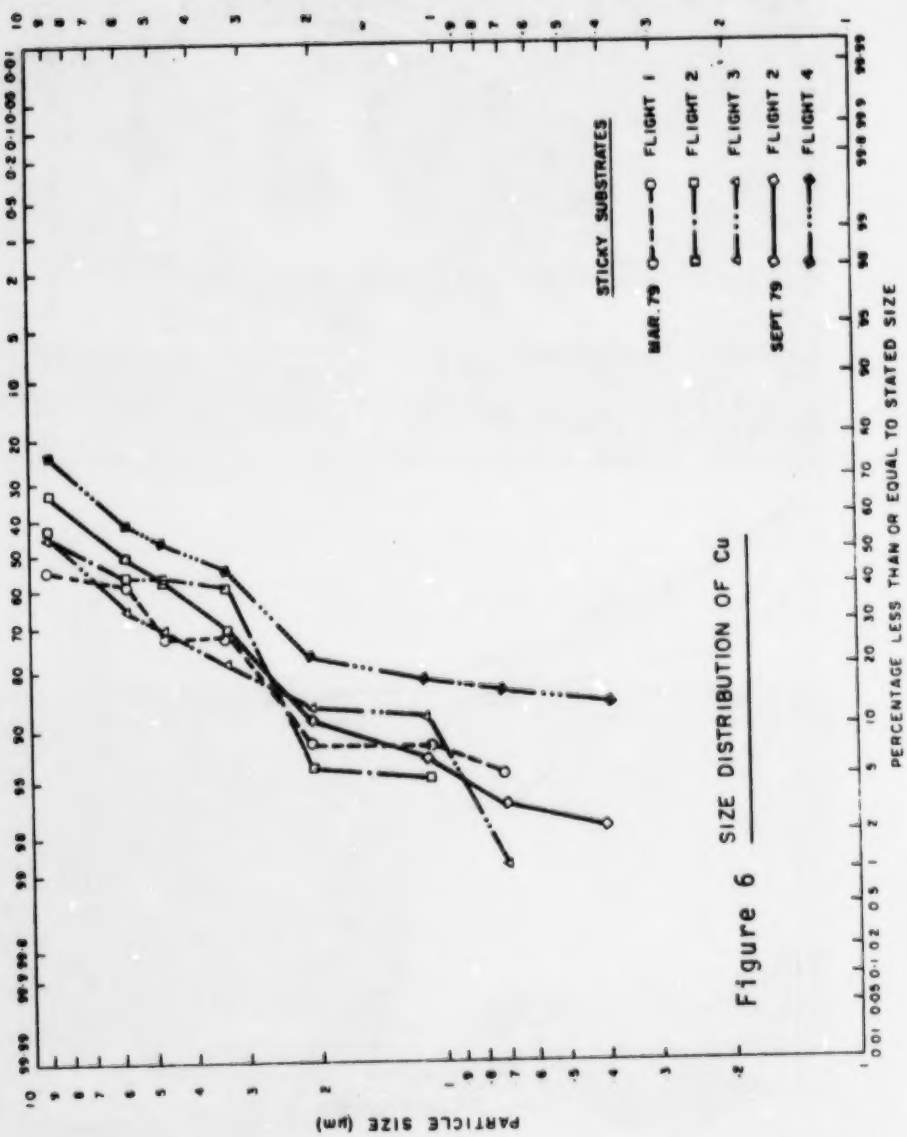


Figure 6 SIZE DISTRIBUTION OF Cu

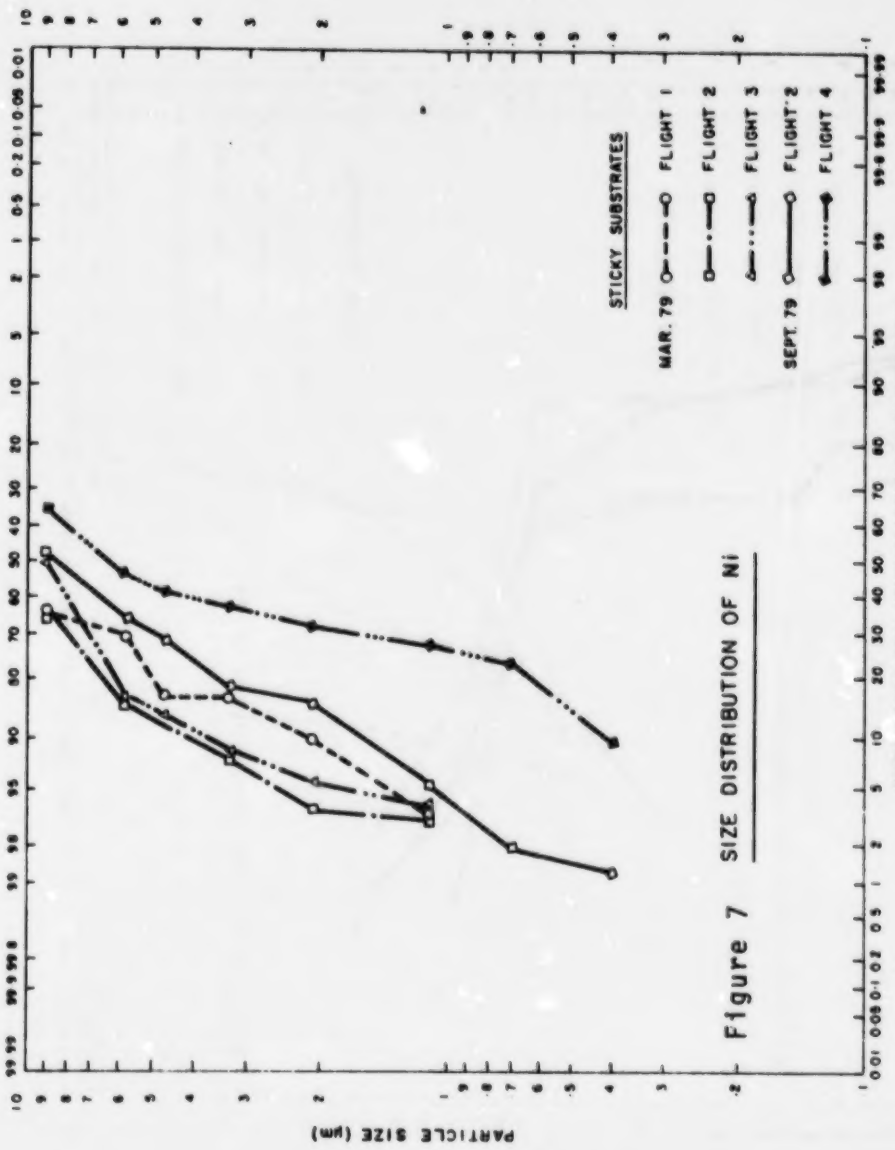


Figure 7 SIZE DISTRIBUTION OF Ni

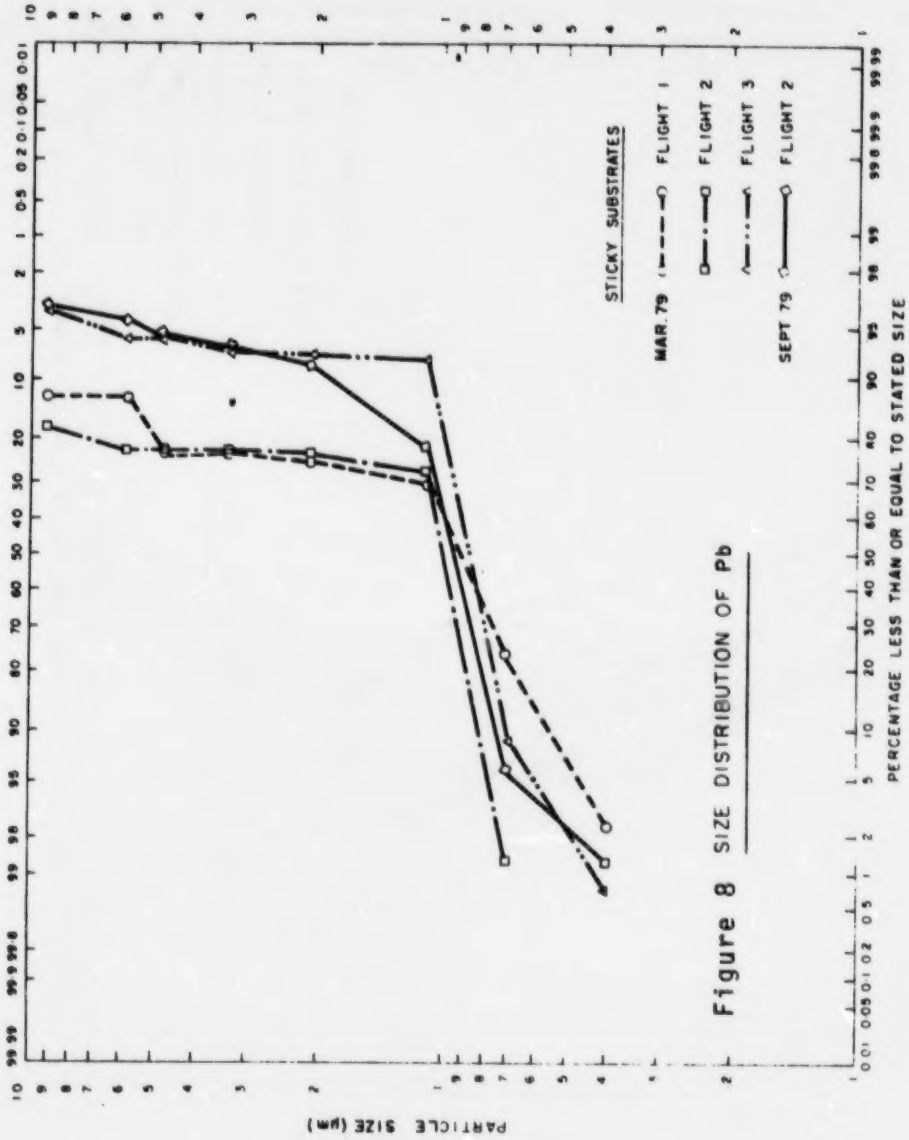


Figure 8 SIZE DISTRIBUTION OF Pb

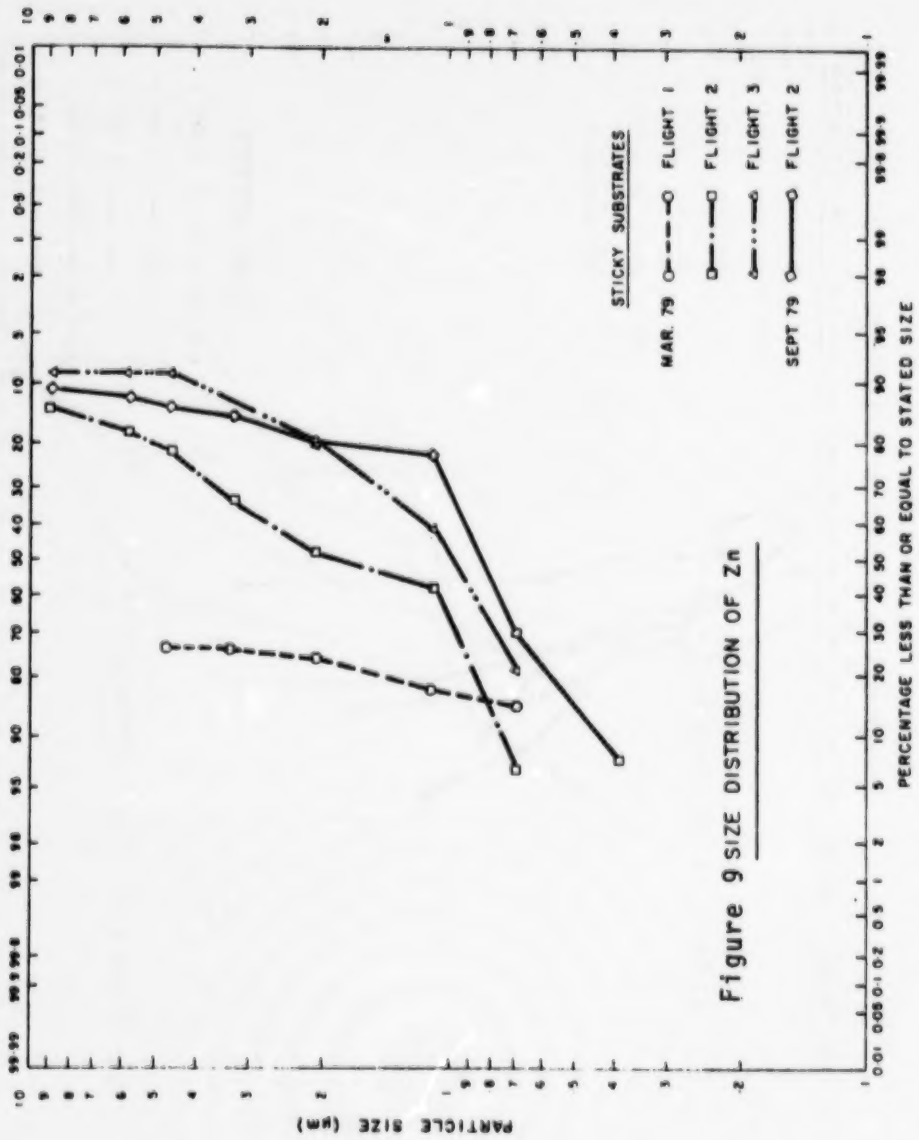


Figure 9 SIZE DISTRIBUTION OF Zn

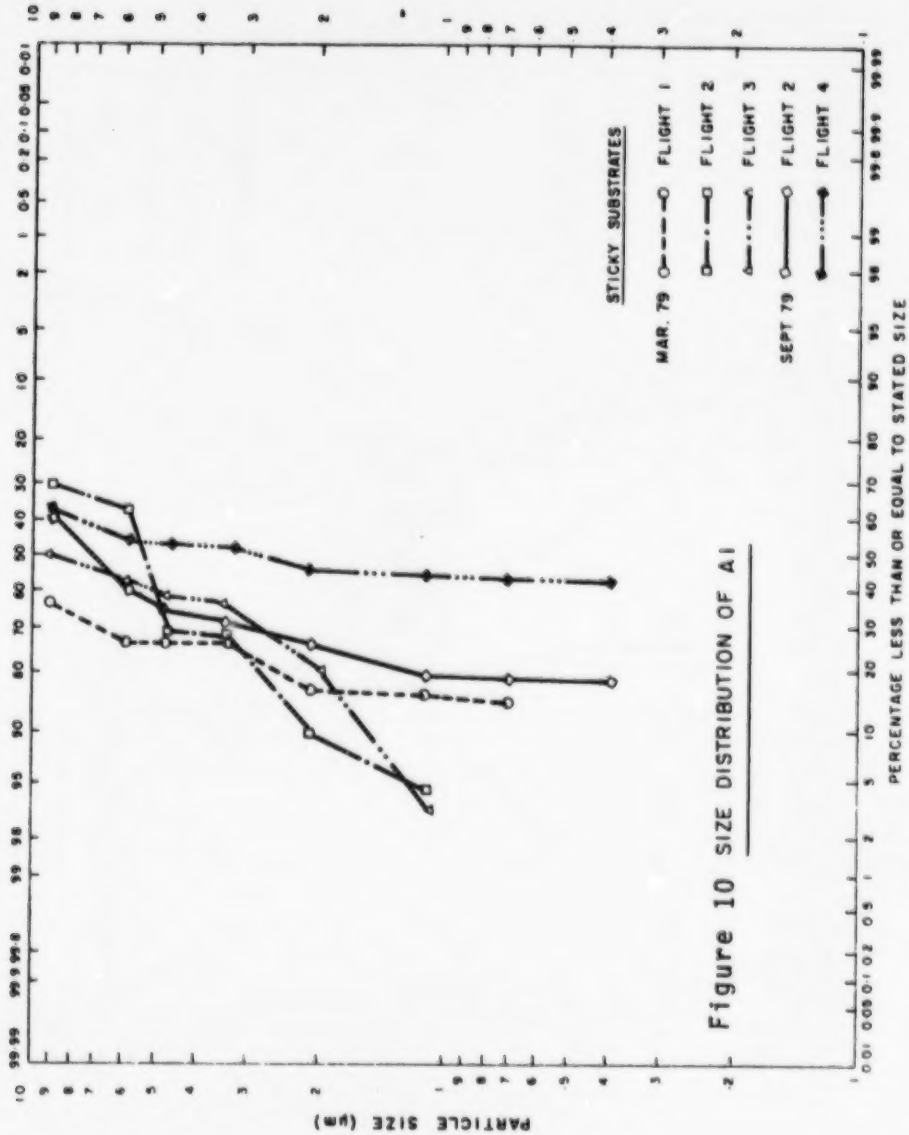


Figure 10 SIZE DISTRIBUTION OF Al

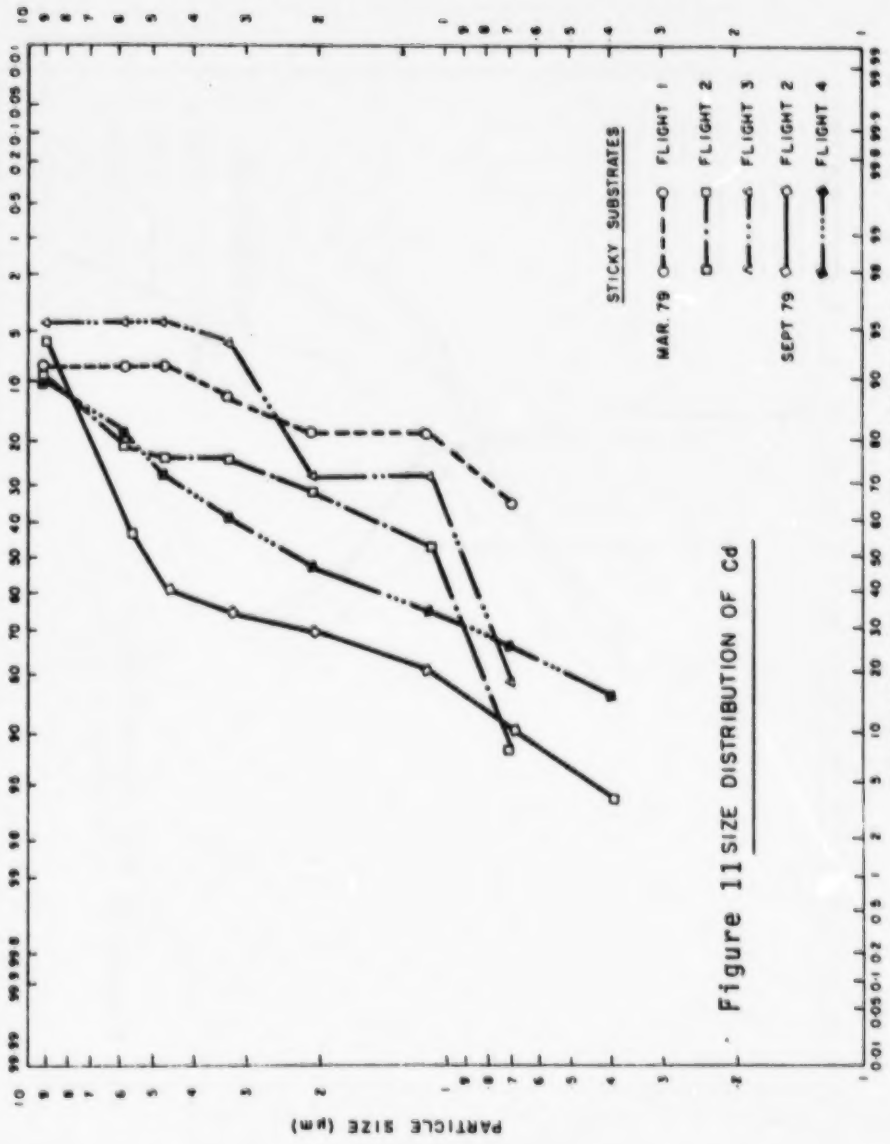


Figure 11 SIZE DISTRIBUTION OF Cd

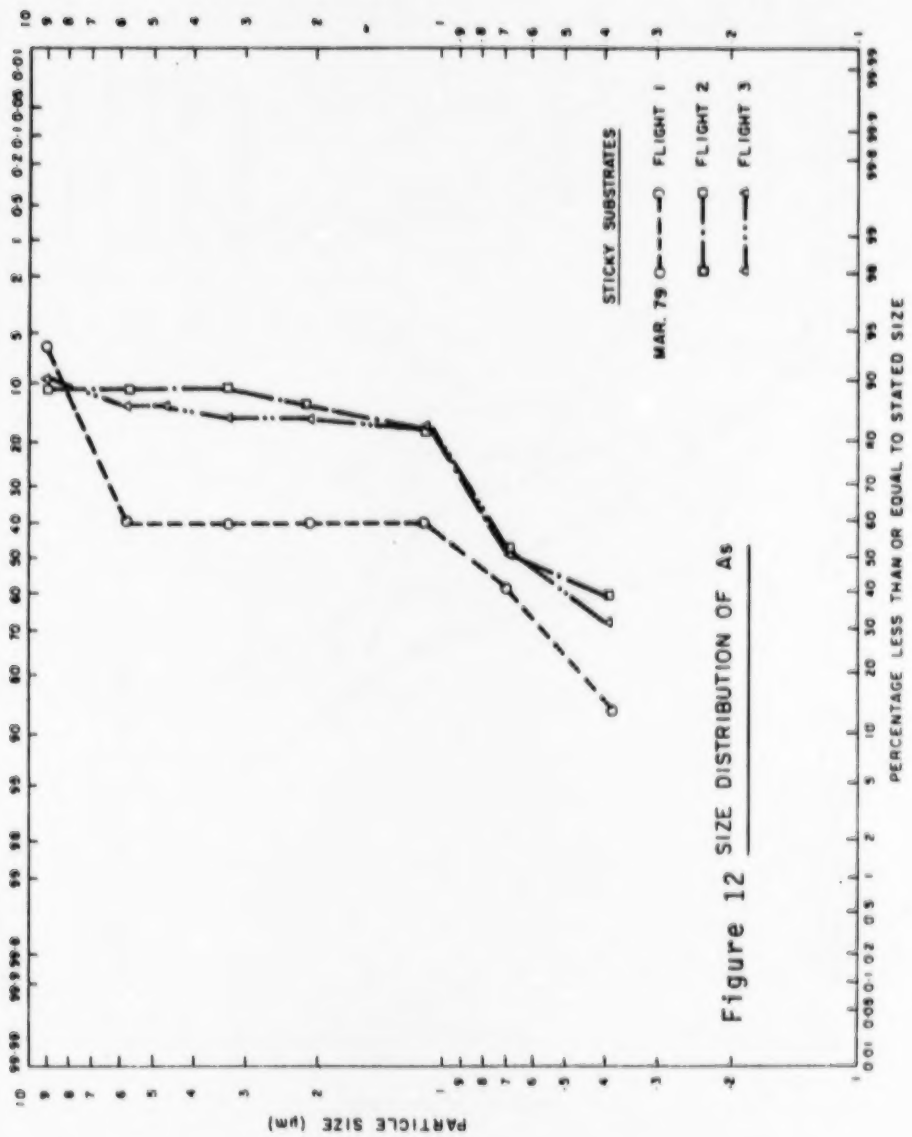


Figure 12 SIZE DISTRIBUTION OF As

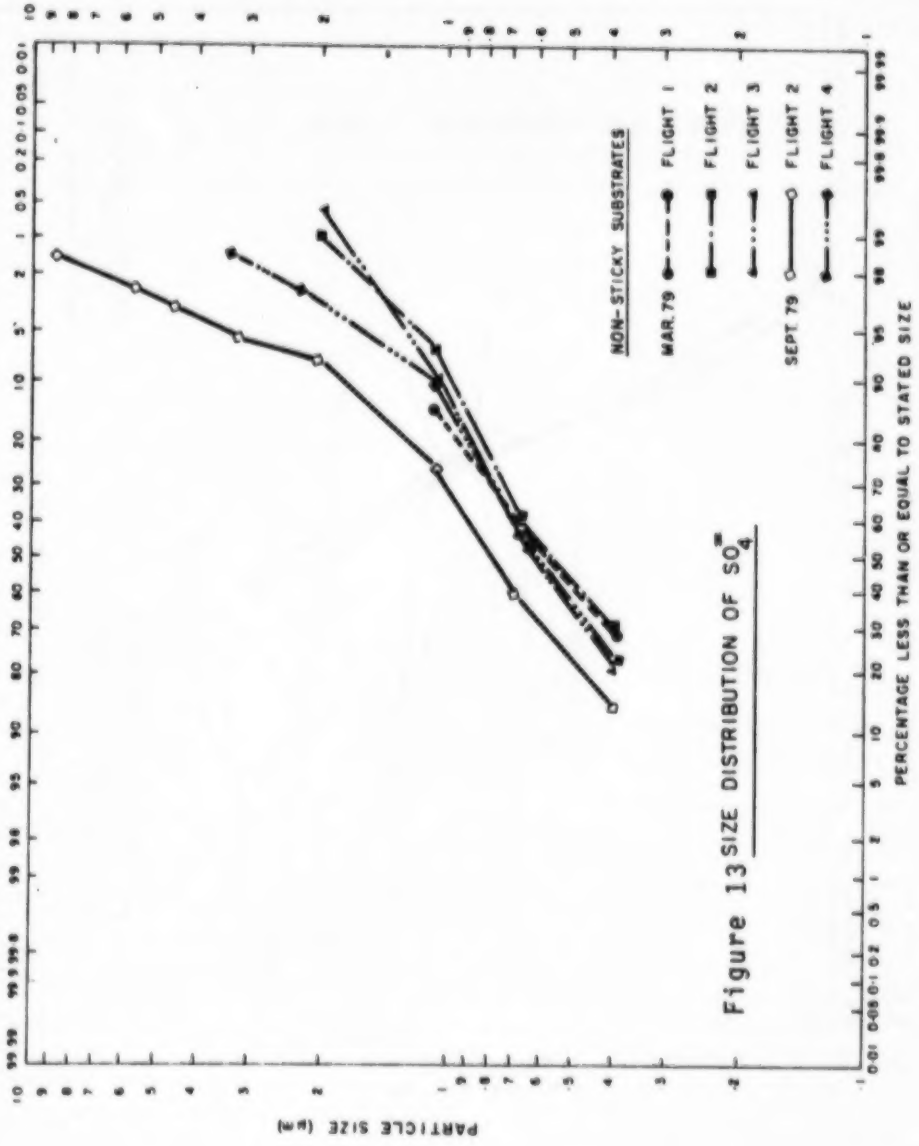


Figure 13 SIZE DISTRIBUTION OF $SO_4^=$

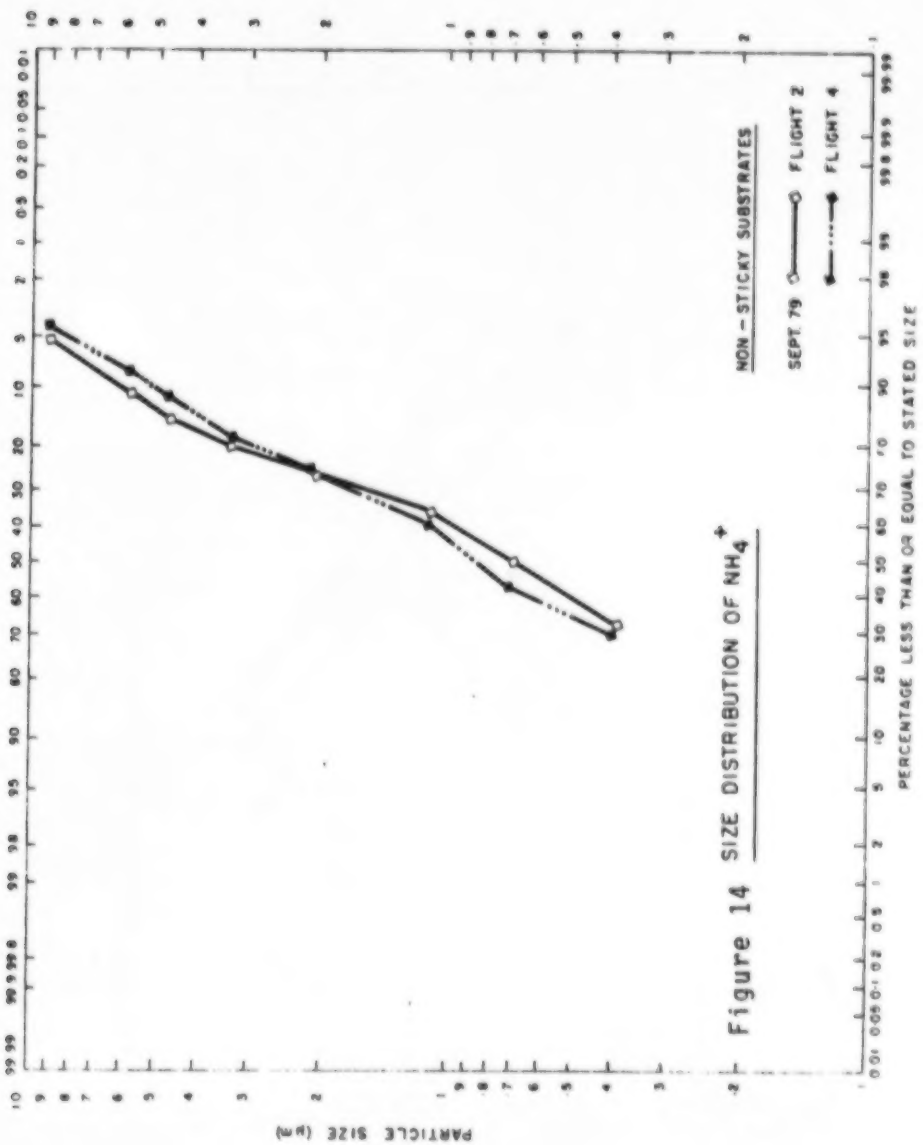


Figure 14 SIZE DISTRIBUTION OF NH_4^+

Figure 15 **MODAL DISTRIBUTION OF Fe**

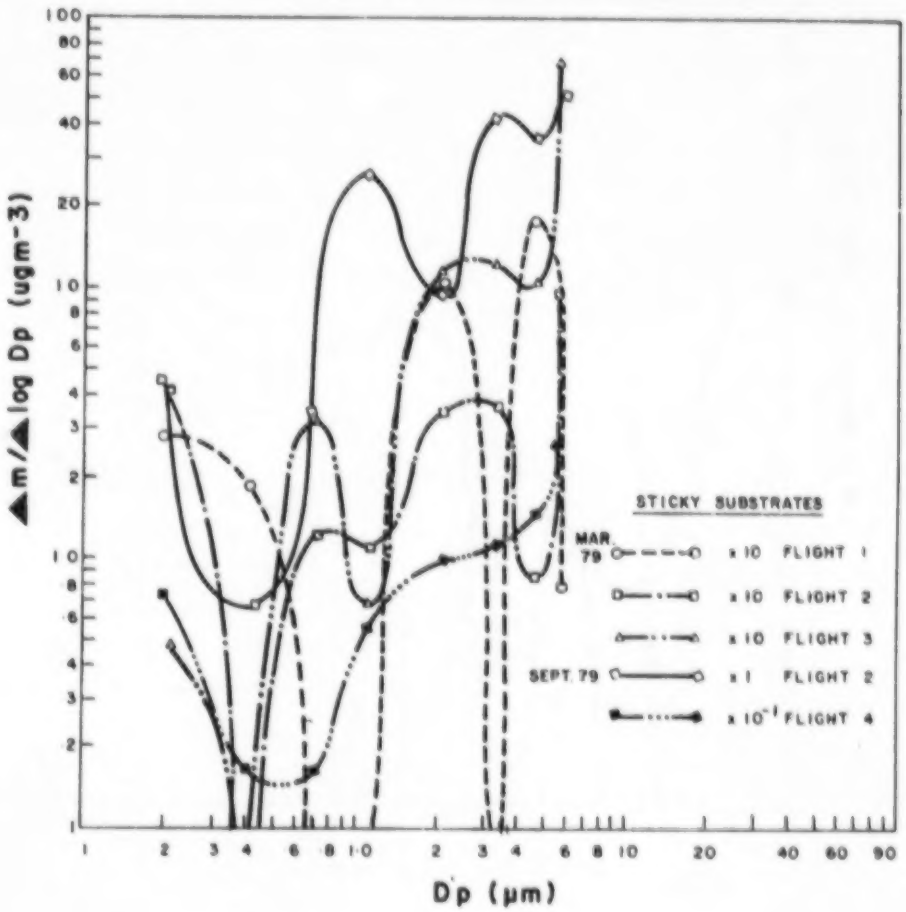


Figure 16 **MODAL DISTRIBUTION OF Cu**

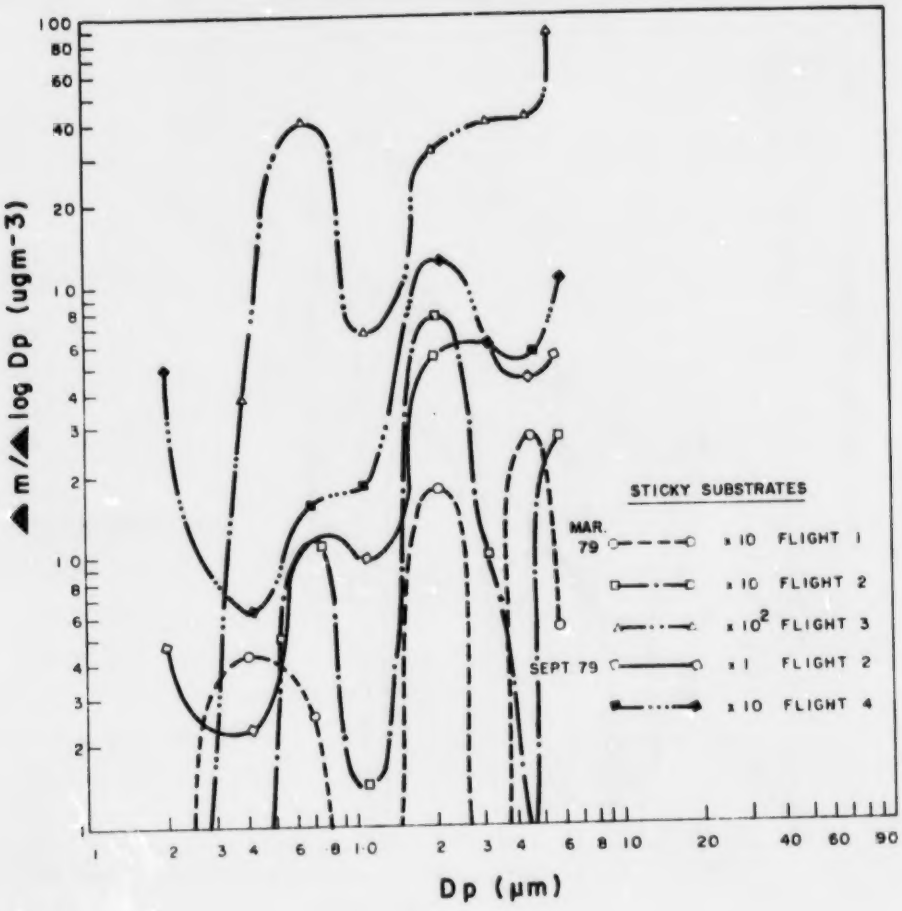


Figure 17 **MODAL DISTRIBUTION OF Ni**

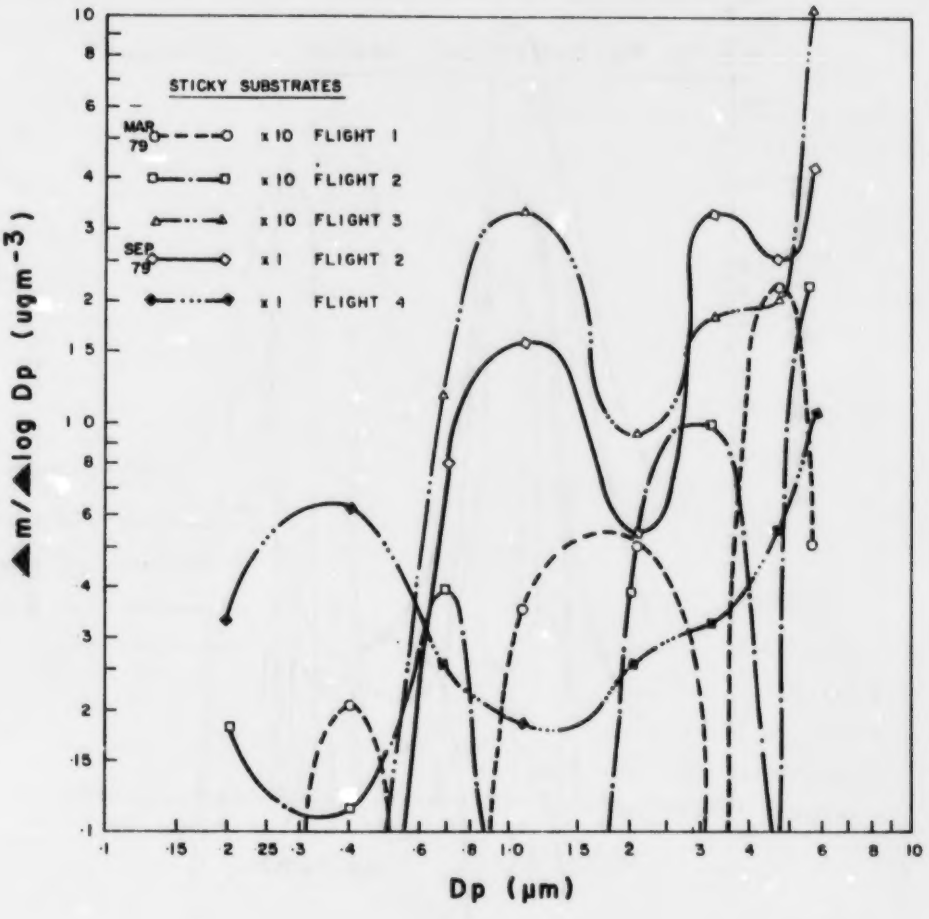


Figure 18 **MODAL DISTRIBUTION OF Pb**

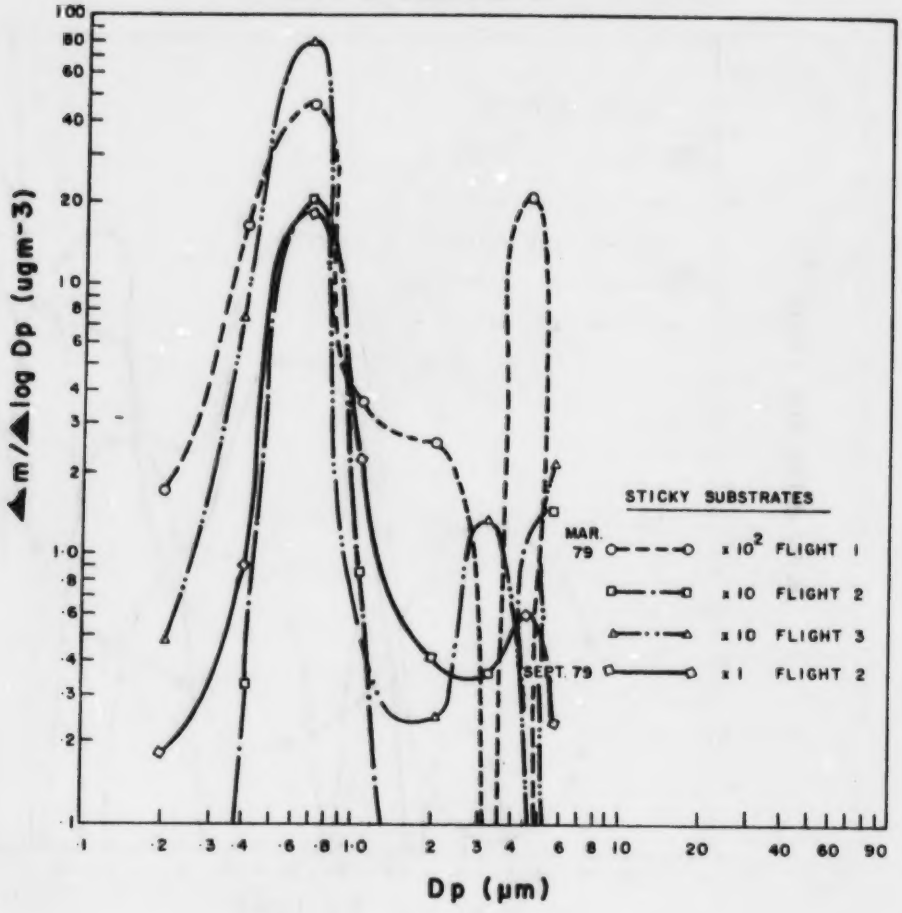


Figure 19 **MODAL DISTRIBUTION OF Zn**

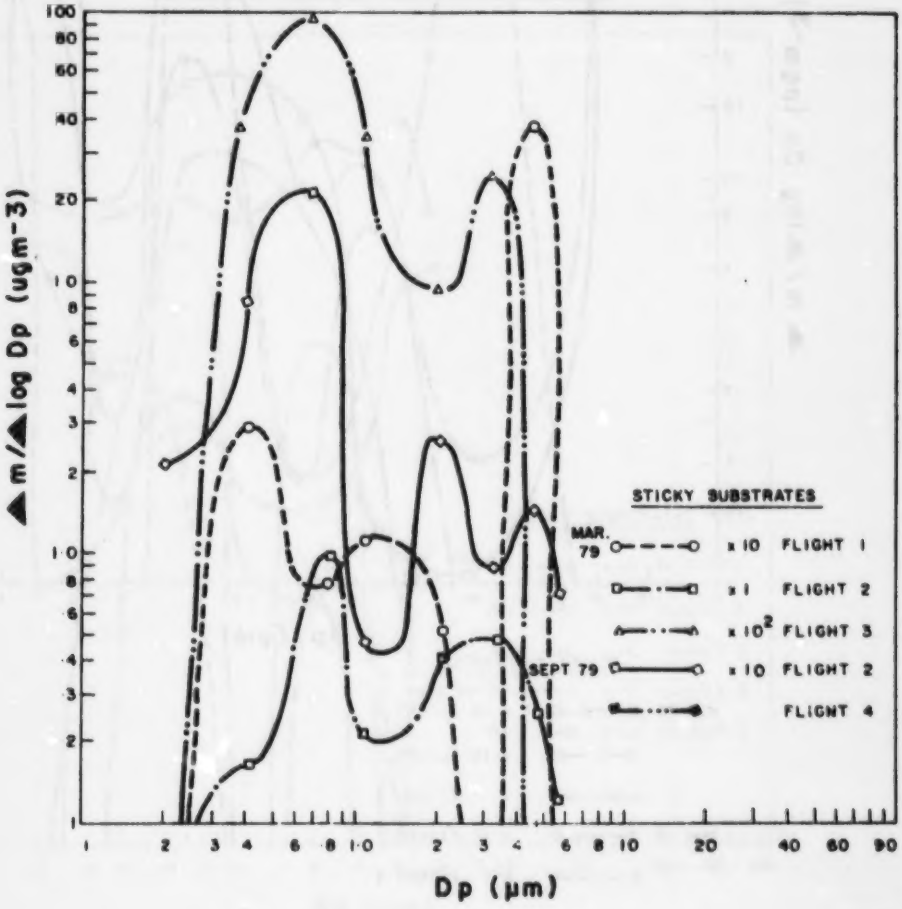


Figure 20 **MODAL DISTRIBUTION OF Al**

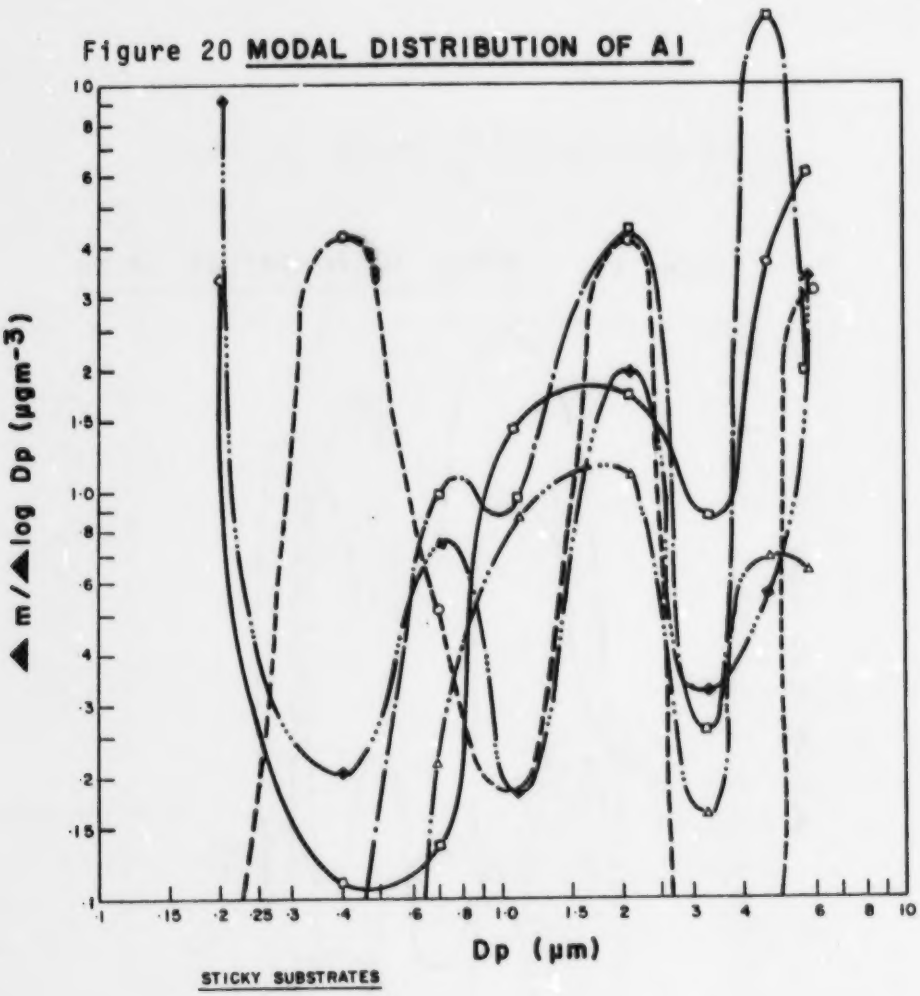


Figure 21 **MODAL DISTRIBUTION OF Cd**

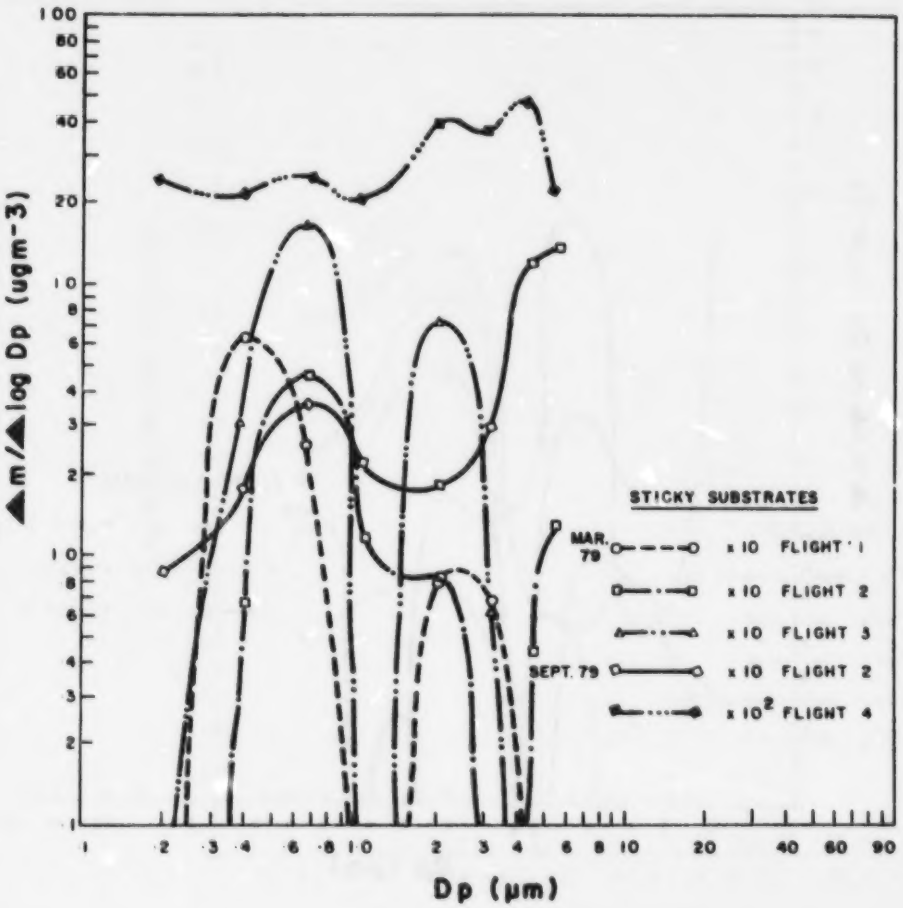


Figure 22 **MODAL DISTRIBUTION OF As**

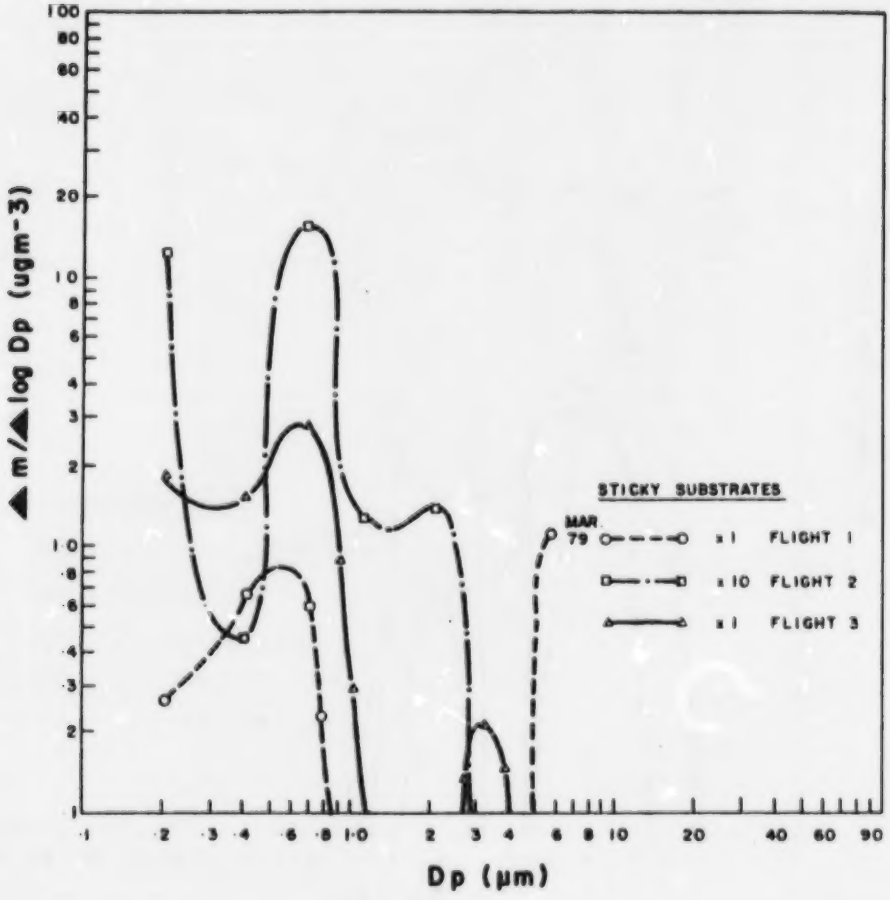


Figure 23 MODAL DISTRIBUTION OF SO_4

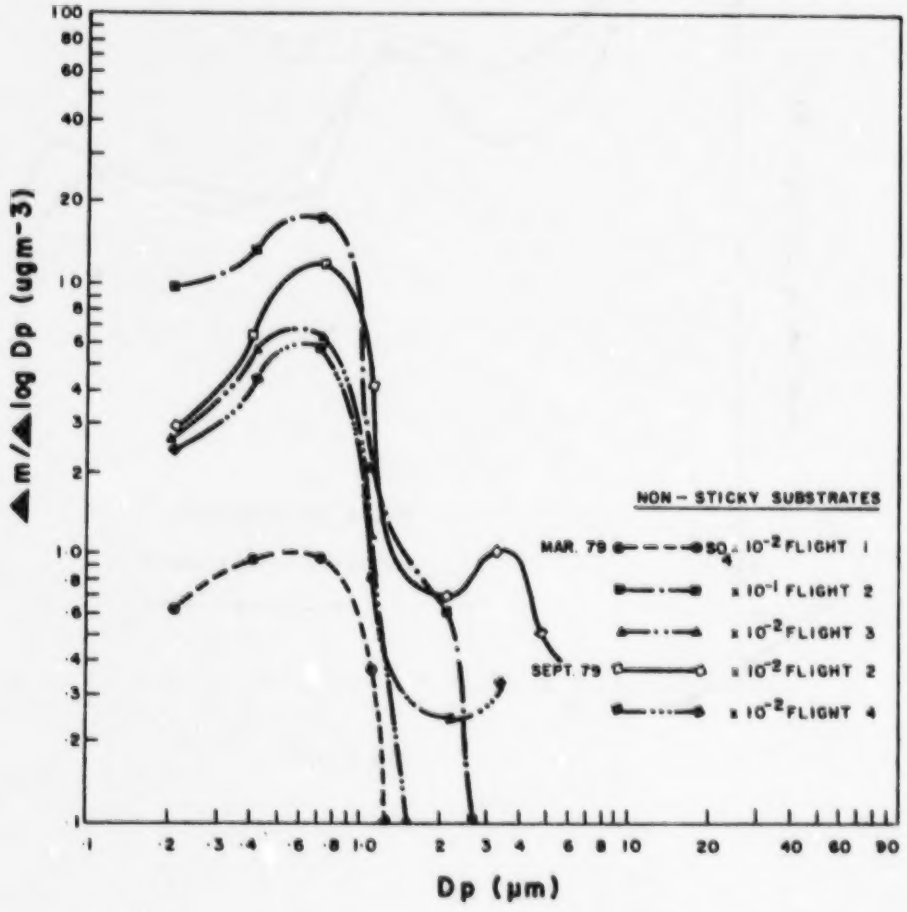
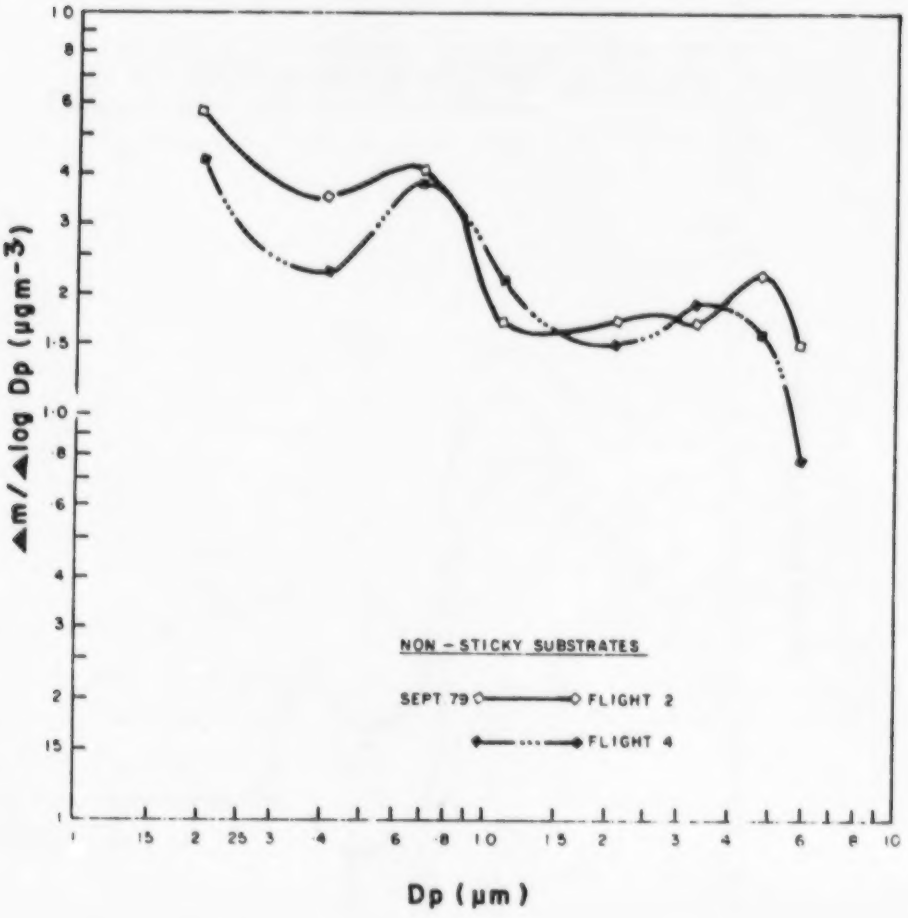


Figure 24 MODAL DISTRIBUTION OF NH_4

(Concentration Expressed in $N-NH_4$)



APPENDIX

Table A1: Flow Volumes (litres) for Individual Flights
March, 1979 Falconbridge Study

Flight#	Run#	47mm Port	47mm Starboard	Andersen Sticky	Andersen Non-Sticky
	1	568	527	1353	1326
1	2	565	511	1306	1288
(Mar. 7)	3	583	466	1320	1288
	Total	1716	1504	3979	3902
	1	637	614	1382	1387
2	2	980	1057	2423	2404
(Mar. 8)	3	605	605	1349	1349
	Total	2222	2276	5154	5140
	1	668	663	1392	1382
3	2	671	660	1509	1483
(Mar. 9)	3	554	585	1282	1251
	Total	1893	1908	4183	4116

Table A2: Flow Volumes (litres) for Individual Flights
September, 1979 Falconbridge Study

Flight#	Run#	47mm Port	47mm Starboard	Andersen Sticky	Andersen Non-Sticky
	1	585	660	1414	1389
1	2	968	1039	2150	2189
(Sept. 9)	3	93	94	202	204
	Total	1646	1793	3766	3782
	1	546	545	1274	1279
2	2	346	302	723	710
(Sept. 11)	3	8.9	9.2	20	20
	Total	900.9	856.2	2017	2009

Table A3: Estimated SO_2 Emission Rates

March, 1979 Falconbridge Study

Flight #	Run #	SO_2 Emission Rate (MT/Day)
1 (March 7/79)	1	268
	2	234
	3	88
2 (March 8/79)	1	199
	2	153
	3	93
3 (March 9/79)	1	221
	2	147
	3	154

Average $\pm$ S.D. = 168 ± 70

Table A4: Estimated SO_2 Emission Rates
September, 1979 Falconbridge Study

Flight	Run#	SO_2 Emission Rate (MT/Day)	Average SO_2 Emission Rate (MT/Day)
1	1	136	
(Sept. 9)	2	248	211*
	3	268	
2	1	288	
(Sept. 11)	2	118	199
	3	199	

Av. $\pm$S.D.=210$\pm$70

*Average SO_2 emission rate which is used in Table 9 (Method 2) calculations. This value is determined by taking into account the number of runs, and the lengths of the runs.

Table A5: Summary of M/Vol Ratios in the Falconbridge Smelter Stack Plume

By 47 mm Filter Packs Sampling - March, 1979*

Flight	Run #	Port Starboard	Parameter (M) (ng/l)										SO_4 (ug/l)	SO_2 (ug/l)
			Fe	Cu	Ni	Pb	Cr	Cd	Co	Se	As	Bi		
	1	P	1.94	0.25	0.39	1.13	-	1.02	-	0.18	0.60	-	0.15	7.50
	2	P	3.33	0.85	0.60	0.88	-	0.28	-	0.18	0.42	-	0.10	4.38
1	3	P	-	0.45	0.31	0.65	-	-	-	0.21	-	-	0.17	8.61
(Mar. 7)	1	S	-	0.68	0.38	1.10	-	-	-	0.27	-	-	0.18	7.44
	2	S	2.27	0.82	0.43	0.98	-	-	-	-	-	-	0.07	5.22
	3	S	-	0.39	0.21	0.56	-	-	-	-	-	-	0.16	8.00
	1	P	1.88	0.53	0.25	1.07	-	0.47	-	-	1.29	-	0.13	14.34
	2	P	5.71	1.37	0.80	2.12	0.04	0.47	0.04	-	1.63	-	0.15	11.36
2	3	P	-	0.43	0.20	0.69	-	-	-	-	0.43	-	0.24	16.00
(Mar. 8)	1	S	1.95	0.55	0.33	1.37	-	0.26	-	-	1.17	-	0.19	14.38
	2	S	5.49	1.49	0.85	2.10	-	0.19	0.04	-	1.31	-	0.16	11.31
	3	S	1.85	0.83	0.23	0.73	-	-	-	-	0.26	-	0.24	15.84
	1	P	10.78	3.59	1.41	8.08	-	1.35	0.06	0.24	5.69	0.39	0.87	54.34
	2	P	-	0.60	0.27	1.55	-	-	-	-	0.95	-	0.32	19.21
3	3	P	1.99	0.76	0.32	1.91	-	0.22	-	-	1.77	-	0.22	26.23
(Mar. 9)	1	S	5.13	3.62	1.03	7.54	-	1.75	-	0.57	7.12	0.48	0.75	53.82
	2	S	1.70	0.79	0.33	3.33	-	3.33	0.06	0.21	1.45	-	0.30	20.52
	3	S	2.39	0.85	0.51	3.42	-	4.07	-	0.24	1.61	-	0.27	27.44

* Only samples with loadings equal to or greater than 2x filter blank values were used in calculations.

Table A6: Summary of M/SO_2 Ratios in the Falconbridge Smelter Stack Plume by 47 mm Filter Pack Sampling - March, 1979*

Flight	Run #	Port/ Starboard	Parameter (M)										
			$Fex10^{-4}$	$Cux10^{-5}$	$Nix10^{-5}$	$Pbx10^{-4}$	$Crx10^{-6}$	$Cdx10^{-4}$	$Cox10^{-6}$	$Sex10^{-5}$	$Asx10^{-5}$	$Bix10^{-5}$	SO_4x10^{-2}
1 (Mar. 7)	1	P	2.85	3.29	5.16	1.50	-	1.36	-	2.35	7.98	-	2.07
	2	P	7.60	19.4	13.7	2.02	-	0.65	-	4.04	9.70	-	2.18
	3	P	-	5.18	3.58	0.76	-	-	-	2.39	-	-	1.9
	1	S	-	9.18	5.10	1.48	-	-	-	3.57	-	-	2.4
	2	S	4.35	15.75	8.25	1.87	-	-	-	-	-	-	1.2
	3	S	-	4.83	2.68	0.70	-	-	-	-	-	-	2.0
2 (Mar. 8)	4	P	1.31	3.72	1.75	0.74	-	0.33	-	-	8.98	-	0.92
	5 & 6	P	5.03	12.03	7.00	1.87	3.59	0.41	3.59	-	14.37	-	1.29
	7	P	-	2.69	1.24	0.43	-	-	-	-	2.69	-	1.49
	4	S	1.36	3.85	2.27	0.95	-	0.18	-	-	8.15	-	1.29
	5 & 6	S	4.85	13.21	7.53	1.85	-	0.16	3.35	-	11.54	-	1.37
	7	S	1.17	5.22	1.46	0.46	-	-	-	-	1.67	-	1.50
3 (Mar. 9)	8	P	1.98	6.61	2.59	1.49	-	0.25	1.10	0.44	10.47	0.72	1.60
	9	P	-	3.1	1.40	0.81	-	-	-	-	4.97	-	1.66
	10	P	0.76	2.89	1.24	0.73	-	0.08	-	-	6.74	-	0.85
	8	S	0.95	6.73	1.91	1.40	-	0.33	-	1.06	13.23	0.90	1.40
	9	S	0.83	3.84	1.62	1.62	-	1.62	2.95	1.03	7.09	-	1.48
	10	S	0.87	3.11	1.87	1.25	-	1.48	-	0.87	5.86	-	0.97
Average			2.59	6.92	3.91	1.22	3.59	0.62	2.75	1.97	8.38	0.81	1.54
Standard Deviation			2.18	4.97	3.35	0.53	-	0.58	1.13	1.33	3.69	0.13	0.44

* Only samples with loadings equal to or greater than 2x filter blank values were used in calculations.

Table A7: Summary of M/Vol Ratios in the Falconbridge Smelter Stack Plume By 47 mm Filter Pack Sampling

September/79*

Flight	Run #	Port Starboard	PARAMETERS (ng/l) Fe	Cu	Ni	Pb	Zn	Al	Mn	Cd	As	Se	$N\text{-}NO_3$	$N\text{-}NH_4$	SO_4 (ug/l)	SO_2 (ug/l)
1	1	P	8.21	1.44	0.75	1.54	-	-	.085	0.32	11.80	0.15	-	-	0.43	31.37
(Sept.9)	2	P	27.17	8.26	3.93	6.61	0.52	3.72	0.10	0.31	36.98	0.15	0.83	2.69	0.77	31.17
	3	P	24.73	9.35	5.05	26.88	-	-	-	0.54	84.95	1.18	53.76	27.96	4.30	198.80
	1	S	7.58	1.35	1.47	1.67	-	2.42	-	0.27	7.58	0.091	-	-	0.35	23.74
	2	S	31.28	7.22	6.93	7.12	0.67	3.27	0.096	0.25	34.46	0.18	0.77	-	0.81	29.83
	3	S	74.47	9.79	5.00	29.79	-	-	-	0.74	82.98	1.06	5.32	31.92	3.94	194.80
2	1	P	7.51	1.14	0.68	2.56	-	-	-	0.16	2.75	.073	-	-	0.24	16.75
(Sept.11)	2	P	11.56	2.43	1.42	4.05	-	-	-	0.17	4.74	0.17	-	-	0.65	51.73
	1	S	9.17	1.36	0.77	2.57	-	-	-	-	3.85	0.055	-	-	0.26	16.78
	2	S	14.24	2.62	1.89	3.97	-	-	-	-	3.54	0.13	-	-	0.61	50.09

* Only samples with loadings equal or greater than 2x filter blank values were used in calculations.

Table A8: Summary of M/SO_2 Ratios in the Falconbridge Smelter Stack Plume by 47 mm Filter Pack Sampling September, 1979*

PARAMETER/SO_2

Flight	Run#	Port	Fe	Cu	Ni	Pb	Zn	Al	Mn	Cd	As	Se	$N\text{-}NO_3$	$N\text{-}NH_4$	SO_4
		Starboard	$X10^{-4}$	$X10^{-5}$	$X10^{-5}$	$X10^{-4}$	$X10^{-5}$	$X10^{-5}$	$X10^{-5}$	$X10^{-4}$	$X10^{-5}$	$X10^{-5}$	$X10^{-5}$	$X10^{-5}$	$X10^{-2}$
1	1	P	2.62	4.58	2.40	.49	-	-	.272	.104	37.6	.490	-	-	1.38
(Sept.9)	2	P	8.72	26.5	12.6	2.12	1.66	11.9	.331	.0994	119	.497	2.65	8.62	2.46
	3	P	1.24	4.71	2.54	1.35	-	-	-	.027	42.7	.595	27.0	14.1	2.16
	1	S	3.19	5.68	6.19	.702	-	10.2	-	.115	31.9	.383	-	-	1.49
	2	S	10.5	24.2	23.2	2.39	2.26	11.0	.323	.0839	115	.613	2.58	-	2.73
	3	S	3.82	5.02	2.57	1.53	-	-	-	.0382	42.6	.546	2.73	16.4	2.02
2	1	P	4.48	6.78	4.05	1.53	-	-	-	.0984	16.4	.437	-	-	1.44
(Sep.11)	2	P	2.23	4.69	2.74	.782	-	-	-	0.335	9.16	.335	-	-	1.26
	1	S	5.47	8.09	4.59	1.53	-	-	-	-	22.9	.328	-	-	1.53
	2	S	2.84	5.22	3.77	.793	-	-	-	-	7.07	.264	-	-	1.22
Average			4.51	9.55	6.47	1.32	1.96	11.03	0.309	0.075	44.43	0.449	8.74	13.04	1.77
Std. Dev.			2.96	8.42	6.63	0.63	0.42	0.85	0.119	0.032	0.036	0.119	12.17	4.00	0.54

* Only samples with loadings equal to or greater than 2x filter blank values were used in calculations.

Table A9: Summary of M/Vol Ratios of the Andersen Substrates+ - March 1979

Flight #	Volume (l)	Stage #	Parameter (M) (ng/l) Fe	Cu	Ni	Pb	Zn	Cr	Cd	Mn	Co	Se	As	Bi	SO_4 (ug/l)
1 (Mar. 7)	3979 (SS)	0	0.52	0.10	0.10	0.03	-	-	0.02	0.02	-	-	0.04	-	-
		1	0.02*	0.01	0.01	-	-	-	-	-	-	-	0.21	-	-
		2	0.17	0.03	0.02	0.02	0.36	-	-	-	-	-	-	-	-
		3	-	-	-	-	-	-	0.01*	-	-	-	-	-	-
	3902 (NS)	4	0.20	0.04	0.01	0.005*	0.01	-	0.015*	-	-	-	-	-	0.01
		5	-	-	0.01	0.01	0.03*	-	-	-	-	-	0.12	-	0.02
		6	-	0.01*	-	0.09	0.02*	-	0.04	-	-	-	0.17	-	0.02
		7	0.05*	0.01	0.005	0.04	0.07*	-	0.16*	-	-	-	0.08	-	0.019
		F	0.085*	-	-	0.005*	-	-	-	-	-	-	0.11	-	-
2 (Mar. 8)	5154 (SS)	0	0.97	0.20	0.13	0.10	0.07	0.003	0.02	0.008	0.0038	-	-	-	-
		1	0.19	0.05	0.04	0.03	0.02*	-	0.02	-	-	-	-	-	-
		2	0.01*	-	-	-	0.02*	-	0.004*	-	-	-	-	-	-
		3	0.06	0.02	0.02	-	0.07	-	-	-	-	-	0.03	-	0.001*
		4	0.07	0.16	0.01	-	0.08	-	0.02	-	-	-	0.03	-	0.006
	5140 (NS)	5	0.03*	0.004*	-	0.01	0.06*	-	0.03	-	-	-	0.32	0.04	0.03
		6	0.02*	0.02	0.01	0.40	0.19	-	0.09	-	-	-	0.11	-	0.03
		7	-	-	-	0.01*	0.04*	-	0.02	-	-	0.03	0.38	-	0.03
		F	0.120*	-	-	-	-	-	-	-	-				
3 (Mar. 9)	4183 (SS)	0	1.67	0.36	0.32	0.08	0.04*	0.03	0.03	0.01	0.01	-	0.17	-	0.002*
		1	1.29	0.17	0.20	0.04	-	0.23	-	0.01	-	-	0.08	-	-
		2	0.10	0.04	0.02	-	-	-	-	-	-	-	-	-	-
		3	0.19	0.06	0.03	0.02	0.04*	-	0.01*	-	-	-	0.03	-	-
		4	0.22	0.06	0.20	0.01*	0.02*	-	0.14	-	-	-	-	-	-
	4116 (NS)	5	0.02*	0.01	0.01	0.01	0.10	-	-	-	-	-	0.04	-	0.04
		6	0.06	0.08	0.02	1.58	0.19	-	0.34	-	-	0.005	0.55	0.22	0.12
		7	-	0.01	-	0.19	0.10	-	0.11	-	-	0.02	0.37	0.03	0.14
		F	0.014*	-	-	0.019*	-	-	-	-	-	0.04	0.55	-	0.02

+ All parameters except SO_4 which was sampled on non-sticky substrate (NS) were sampled on sticky substrate.
* Sample loading less than 2 x filter blank value.
- Below detection limit.

Table A10: Summary of (M/Vol) Ratios of the Andersen Substrates[+]
September, 1979

Flight#	Volume (l)	Stage#	PARAMETERS (ng/l) Fe	Cu	Ni	Pb	Zn	Al	Mn	Cd	$N\text{-}NH_4$	SO_4 (ug/l)
1 (Sept. 9)	3766 (SS)	0	21.85	2.05	2.31	0.19	0.96	2.34	.042	0.40	0.24	.010
		1	10.09	1.06	0.85	0.53	-	1.20	.029	0.27	0.29	.008
		2	3.32	0.40	0.24	.053	-	0.35	.008*	0.11	0.21	.005
		3	7.04	0.93	0.53	.053	-	0.13*	.008*	.045	0.26	.015
	3782 (NS)	4	1.86	1.06	0.11	.080	.050	0.35	.013	.035	0.34	.013
		5	7.83	0.27	0.45	0.64	-	0.40	.008*	.061	0.48	0.12
		6	0.61	0.21	0.16	3.66	0.45	-	.008*	.072	0.79	0.23
		7	0.16*	.053	-	0.21	0.21	-	.003*	.042	0.85	0.16
		F	1.38	0.13	.053*	.053	.066	1.01	.029	.027	1.72	.087
2 (Sept. 11)	2017 (SS)	0	8.43	0.25	0.40	0.050	0.69	2.38	.015*	0.050	0.20	-
		1	4.12	0.20	0.20	-	-	.64	-	.045	0.15	-
		2	1.29	.050	-	-	-	-	-	.045	0.15	-
		3	1.64	0.99	-	.050	-	-	-	.055	0.30	.0047
	2009 (NS)	4	1.93	0.25	-	-	-	0.40*	-	.079	0.30	.0047
		5	1.49	.050	-	-	-	-	-	0.060	.60	0.023
		6	0.30*	.030*	0.050*	1.04	.030	0.15*	-	.050	0.75	.107
		7	0.40	-	0.15	-	-	-	-	0.055	0.55	.113
		F	2.13	0.15	.099*	0.15	-	2.73	.045	0.74	1.29	.071

[+] All parameters except $N\text{-}NH_4$ and SO_4 which were sampled on non-sticky substrate (NS) were sampled on sticky substrate (SS).

* Sample loadings less than 2x filter blank values.

\- Below dectection limit.

Table A11: Summary of the Observed Particle Size and Expected Effective Cut-Off Diameter (in um)

Stage Number	50% Effective Cut-Off Diameter	Approximate Observed Diameter
0	9.0	36
1	5.8	-
2	4.7	-
3	3.3	11
4	2.1	4
5	1.1	7
6	0.7	500 - 700
7	0.4	4 - 28
F	0.2[+]	-

[+] assumed to be $\frac{0.4 - 0.0}{2} = 0.2$